"Design and characterization of biomass derived adsorbents for the Adsorptive desulfurization of liquids fuels"

Dissertation submitted to

Visvesvaraya National Institute of Technology, Nagpur

In partial fulfilment of the requirements for the award of the degree

Master of Science

In

Chemistry

by

Swati Kamble (MS23CHM010)

under the guidance of

Dr. Sorokhaibam Laxmi Gayatri

Department of chemistry

Visvesvaraya National Institute of Technology

Nagpur 440010 (India)

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Declaration

I, **Swati Suresh Kamble**, hereby declare that this dissertation titled **"Design and Characterization of Biomass Derived Adsorbents for the Adsorptive Desulfurization of liquids fuels"** is carried out by me in the department of chemistry of Visvesvaraya National Institute of Technology, Nagpur. The work is original and has not been submitted earlier whole or in part for the award of any degree at this or any other institute / university.

Name and signature

Date:

Certificate

This to certify that the dissertation titled **"Design and Characterization of Biomass Derived Adsorbents for the Adsorptive Desulfurization of liquids fuels"** is submitted by **Swati Suresh Kamble** in partial fulfilment of the requirements for the award of the degree of **Master of Science in Chemistry** VNIT Nagpur. The work is comprehensive, complete and fit for final evaluation.

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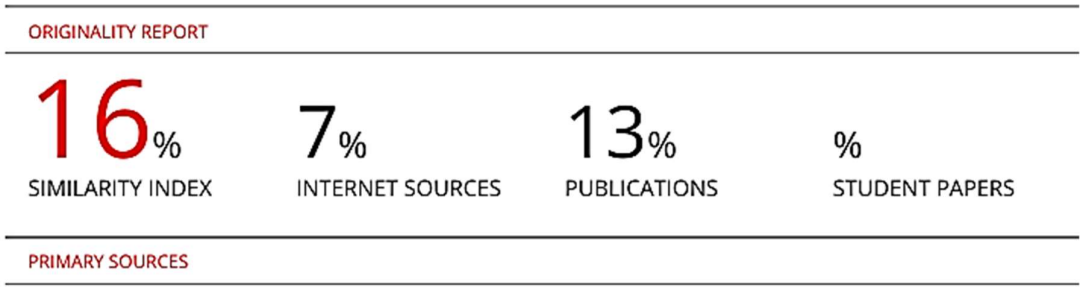
NAGPUR

Certified that M.Sc. Dissertation titled submitted by Swati Kamble **"Design and Characterization of Biomass Derived Adsorbents for the Adsorptive Desulfurization of liquids Fuels"** Enrollment No. MS23CHM010 ID No. 30545 has been checked for plagiarism using TURNITIN software and the overlap is found within the prescribed limits. A summary of the report is given below:



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Date:

Place: VNIT, Nagpur

ABSTRACT

Burning fossil fuels in power plant, industries and vehicles releases sulfur oxides (SO_x) into the atmosphere. The formation of sulfur oxide during combustion leads to acid rain, deforestation, air pollution, ozone layer depletion and severe smog. Also, sufur compounds in liquid fuels can cause engine corrosion and deactivate catalysts by adsorbing on the catalyst surface, blocking active and hindering its ability to convert pollutants like carbon monoxide, hydrocarbon and nitrogen oxides. This can be leads to reduced catalyst efficiency and increased emissions. Thus, the amount of sulfur compounds in liquid fuels creates major operational and environmental issues. To this problem, governments around the world have implemented strict regulations that the limit of sulfur content in liquid fuels be less than 10 ppm. Effective desulfurization techniques can be utilized to reduce the sulfur content in fuels. In this study, activated carbon was developed from biomass ***Euryale ferox*** (named as FAT). Carbonaceous adsorbent further was modified with titanium to developed Ti@FAT to improve its adsorption capacity. *Euryale ferox* activated carbon was prepared by carbonization and chemical activation and modified with titanium by using co-precipitation method. These materials were developed for investigating the removal of sulfur using DBT (dibenzothiophene) as model oil in iso-octane. FAT and synthesized Ti@FAT were characterized by techniques, such as PXRD (powered X-Ray diffraction), FTIR (Fourier-transform infrared spectroscopy), BET (Brunauer-Emmett-Teller), TGA (Thermogravimetric analysis), and SEM-EDS (Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy). PXRD data revealed the amorphous nature of FAT and slight crystalline nature of Ti@FAT. FTIR shows availability of multiple surface functional groups such as C-O, C=C, -OH, O=C=O. BET analysis shows the surface area of FAT and Ti@FAT is 1400 m^2/g and 1095 m^2/g respectively**.** TGA analysis shows thermal stability of Ti@FAT weight loss is 3% and FAT weight loss is 23%. Batch adsorption studies were carried out by using 200 ppm model fuel to determine the effect of adsorbent dosage, concentration, time, temperature. The optimum parameters for desulfurization were found at a dosage of 0.02g/L in 10ml of fuel. Adsorption capacity of adsorbents for desulfurization of DBT was observed in the following order: Ti@FAT (64.3 mg/g) > FAT (57.8 mg/g). The analysis of multicomponent stimulated fuels (MSMF) by using GC-FPD (gas chromatography-Flame photometric detector) revealed substantial removal of different types of sulfur such as thiophene, dibenzothiophene, 4, 6-dimethyldibenzothiophene, respectively.

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NOMENCLATURE

AC	Activated Carbon
ADS	Adsorptive Desulfurization
BS VI	Bharat Stage VI
TH	Thiophene
Ti@FAT	Titanium modified FAT
BDS	Bio-desulfurization
BT	Benzothiophene
DBT	Dibenzothiophene
4,6-DMDBT	4,6- Dimethyldibenzothiophene
H_2S	Hydrogen sulfide
MOF	Metal Organic Frameworks
NADH	Nicotinamide -adenine dinucleotide
ODS	Oxidative desulfurization
Ppm	Parts per Million
rpm	Rotations per Minute
RH	Alkanes
RSH	Mercaptans
R-S-R	Sulfide
R-S-S-R	Disulfide
SCCs	Sulfur containing compounds
SO_2	Sulfur dioxide
USEPA	United States Environmental Protection Agency
MSMF	Multicomponent simulated model fuel

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The atmosphere contains a number of naturally occurring greenhouse gases, including CO, CO_2, NO_X, SO_X, water vapour and methane. However, the emission of these greenhouse gases into the atmosphere has rapidly increased due to a variety of variables, including human activities, the convenience of transportation facilities, and multiple industry operations. Despite this, there are still health risks and environmental effects associated with SO_x. Numerous sulfur compounds used in transportation fuels cause SO_X when they burn. Long hydrocarbon chains found in fossil fuels like gasoline and diesel are the main source of CO_2 emissions into the atmosphere.[1]

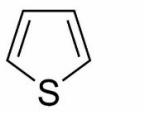
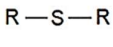
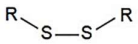
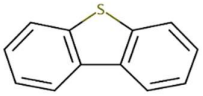
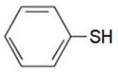
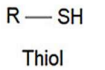
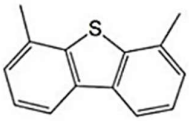
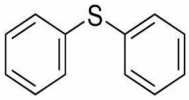
There one of the main causes of climate change, global warming, natural disasters, and the challenges facing life is the atmosphere's high concentration f SO_X and CO_2. Numerous techniques, including bio-desulfurization (BDS), oxidative desulfurization (ODS), extractive desulfurization (EDS), adsorptive desulfurization (ADS), and Hydrodesulfurization (HDS), have been documented for the desulfurization of fossil fuels.[2] HDS is regarded as the most well-known and traditional approach among all of these strategies. It is commonly known that sulfur contributes to smog, acid rain, climate change, reduced combustion engine efficiency, and corrosion of metal parts. The adsorption process is one of the most widely used technique for reducing CO_2 and SO_X levels because of its low environmental impact, ease of operation in ambient conditions, low energy, consumption and other factors that make it an overall cost-effective process. Conversely, the primary disadvantages of using an adsorbent that its selectivity. However, by adjusting their structural characteristics, such as particular surface area, porosity and surface functioning it can be improved.

1.1.1 Types of Sulfur compounds in liquid fuels

Crude oil obtained from various oil fields contains sulfur-based compounds that differ in both type and concentration. Typically, heavier crude oils have a higher sulfur content and more complex sulfur species compared to lighter ones. These sulfur compounds are generally classified into two main categories based on their chemical nature: organic and inorganic sulfur. Inorganic sulfur in crude oil appears as hydrogen sulfide (H_2S), elemental

sulfur, and pyrites. Organic sulfur compounds, on the other hand, include thiols, Sulfides, thiolanes, thiophenes, benzothiophenes, dibenzothiophenes, and their alkylate counterparts.[3] In the organic form, sulfur is bonded within hydrocarbon molecules as a heteroatom. While refinery processes effectively remove most of the inorganic sulfur, many organic sulfur compounds persist in the refined products. As a result, both types of sulfur compounds can still be found in various fuel fractions after crude oil is processed.

Table 1.1 Types of Sulfur in liquid Fuels [3]

Refractory sulfur compounds	Others sulfur compounds
 Thiophene	 Sulfide  Disulfide
 Dibenzothiophene	 Thiophenol  Thiol (Mercaptan)
 4,6-Dimethyldibenzothiophene	 Diphenyl sulfide

1.2 Importance of desulfurization

The concentration of sulfur compounds in the atmosphere has risen sharply due to the increased consumption of fossil fuels and widespread industrialization across much of the world. Even with technological improvements and stricter regulations, emissions from

burning petroleum-based fuels remain a significant contributor to air pollution. The continuous release of sulfur oxides (SO_x), nitrogen oxides (NO_x), and particulate matter negatively affects ecosystems, public health, and the quality of life, particularly for people living in urban areas. [4]These processes are critically important both environmentally and industrially because they provide most of the sulfur needed for industrial purposes, such as in the Claus and contact processes. By producing sulfur-free compounds essential for various catalytic applications, they not only meet industrial demands but also help minimize the emission of hazardous sulfur compounds into the environment

1.2.1 Harmful effects of sulfur in liquid fuels

Sulfur in liquid fuels immediately causes the release of SO_2 and sulfate particulate matter (SPM), which put at risks public health and community while also reducing engine life due to corrosion. Vehicle emissions have a significant impact on air quality. Combustion converts sulfur compound to sulfur oxides, which eventually produce acid rain. Sulfur oxide and other combustion byproducts from sulfur containing compounds cause environmental problem such as smog, global warming and water contamination. Even with more strict heavy duty, highway engine rule, this engine will continue to produce significant volume of nitrogen oxide and particulate matter both of which lead to substantial public health issues. The particulate matter found in diesel exhaust is expected to cause high level of lung cancer people. Other health consequences include worsening respiratory and cardiovascular disorders, exacerbating existing asthma, chronic bronchitis and reducing lung function. Desulfurization of fuels is therefore extremely important in the petroleum industry. [5]

1.2.2 Stringent regulations to curb sulfur emission

The International Maritime Organization recommended lowering the sulfur content of marine fuel from 3.5% to 0.5% in order to lower ship emissions the clean air act sets nationwide limitation on sulfur dioxide particularly form coal-fired power plants.[6] The European union industrial emission directive restricts SO_2 emission from manufacturing sources across the European union. Many countries require ultra-low sulfur diesel and gasoline to limits the automobile emission. Industries such as metal smelting, cement and

chemical manufacture have severe SO_2 emission limitations. Dry sorbet injection, wet scrubbers, and process modification are among the technologies used to reduce the amount of sulfur in raw materials.[7]

1.Global regulatory trends

Government and international authorities are strengthening limits on sulfur emissions, particularly sulfur dioxide due to its significant influence on air pollution, acid rain and public health. The following table show global regulatory trends table 1.1

Table 1.2 Global regulatory trends [8]

Region / Scope	Fuel Type	Sulfur Limit (Recent)	Key points
European Union (EU)	Gasoline, diesel (road)	Max **10 ppm sulfur** (since ~2009, "sulfur-free fuels")	Focus shifting to renewable fuels, e-fuels, and CO_2 intensity reductions.
	Marine fuels	**0.5%** globally, **0.1%** in ECAs	IMO-aligned; stricter in Baltic, North Sea, and inland waterways.
United States (U.S.)	Gasoline	Avg **10 ppm** (Tier 3 standards, since 2017)	Nationwide; enables better vehicle emission controls.
	Diesel (ULSD)	Max **15 ppm sulfur** (since ~2006)	Fully phased in for on-road, non-road.
	Marine fuels	**0.5%** globally, **0.1%** in ECAs	IMO-aligned; additional state-level restrictions in California.
China	Gasoline, diesel (road)	Max **10 ppm** (since ~2019)	Nationwide implementation; focus now

			expanding to trucks, off-road, and shipping sectors.
	Marine fuels	**0.5%**, moving to **0.1%** in ECAs	Yangtze, Pearl, Bohai seas; domestic ECA enforcement.
Africa, Southeast Asia, Latin America	Diesel, gasoline (varied)	Transitioning from **500–10,000 ppm** to **50–10 ppm**	UNEP sulfur reduction programs helping phase out high-sulfur diesel; progress uneven by country.
Global (Marine Shipping)	Heavy fuel oil (bunker fuel)	**0.5%** globally (IMO 2020); **0.1%** in ECAs	Scrubber use widespread but under environmental scrutiny; shift toward alternative fuels underway.

2.Indian standards

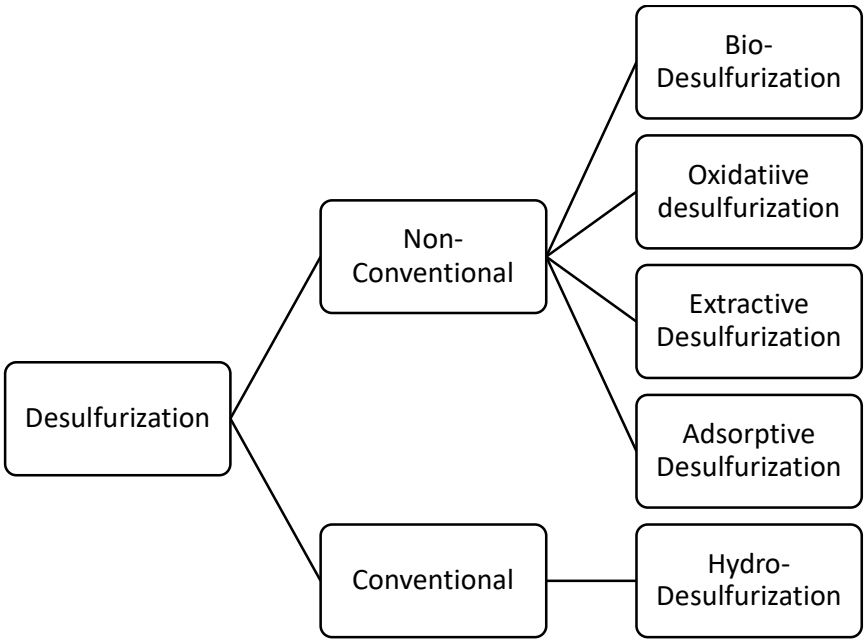
India has made tremendous progress toward reducing sulfur emissions from liquid fuels, particularly in the transportation sector. The most significant shift occurred with the implementation of the Bharat stage VI fuels and vehicle norms which went into force countryside in April 2020.

Table 1.3 Sulfur Reduction Act in India[9]

Year	Standard	Sulfur concentration in Gasoline (ppm)	Sulfur concentration in Diesel (ppm)
2005	BS2 BS3	500ppm (nationwide) 350ppm (selected cities)	500ppm (nationwide) 350ppm (selected cities)
2010	BS3 BS4	350ppm (nationwide) 50ppm (selected cities)	150ppm (nationwide) 50ppm (selected cities)
2017	BS4	50ppm (nationwide)	50ppm (nationwide)
2020	BS6	10ppm (nationwide)	10ppm (nationwide)

1.3 Desulfurization Techniques

Desulfurization is a process that involves removing sulfur or sulfur-containing compounds from fuels or industrial gases to prevent the emission of sulfur dioxide (SO_2). This step is essential because burning sulfur results in the formation of SO_2.[10] In petroleum refineries, desulfurization plays a central role. Currently, Hydrodesulfurization (HDS) is the most widely used technique for eliminating sulfur compounds. Other notable methods include Extractive desulfurization, Adsorptive desulfurization (ADS), Biodesulfurization (BDS), Oxidative desulfurization (ODS), among others Some sulfur-containing compounds in liquid fuels illustrate the various technologies



employed for desulfurization**.**

Fig 1.1 Desulfurization Technologies

Hydrodesulfurization is the most common method used in industries today.[11] It is used for treating petroleum fraction by removing sulfur compounds like sulfur dioxides and sulfides. HDS is typically maintained a temperature between 300 to 400^0c and hydrogen pressure of 5 to 13 Mpa. Model compound studies revel two distinct routes for HDS reaction. The HDS-DBT Mechanism. The first technique direct involve removing sulfur atom from DBT molecules, resulting in biphenyl. The second route includes partially hydrogenating DBT molecule before hydrogenolysis to eliminate sulfur from the C-S link. The following steps shows the reaction takes place during HDS.

1.3.2 Mechanism of Hydrodesulfurization

Hydrodesulfurization catalysts are typically Co or Ni- Promoted Mo or W sulfide. The standard support material for HDS catalysts is γ-Al2O3, which has a high surface area and great thermal and mechanical stability.[12] The HDS technique is widely used in refineries worldwide, however it has inherent limitations. This technique is costly because to its high

temperature and pressure requires. The significant consumption of pricey hydrogen raises running costs. Fig 1.2 shows the HDS Method of Desulfurization process.

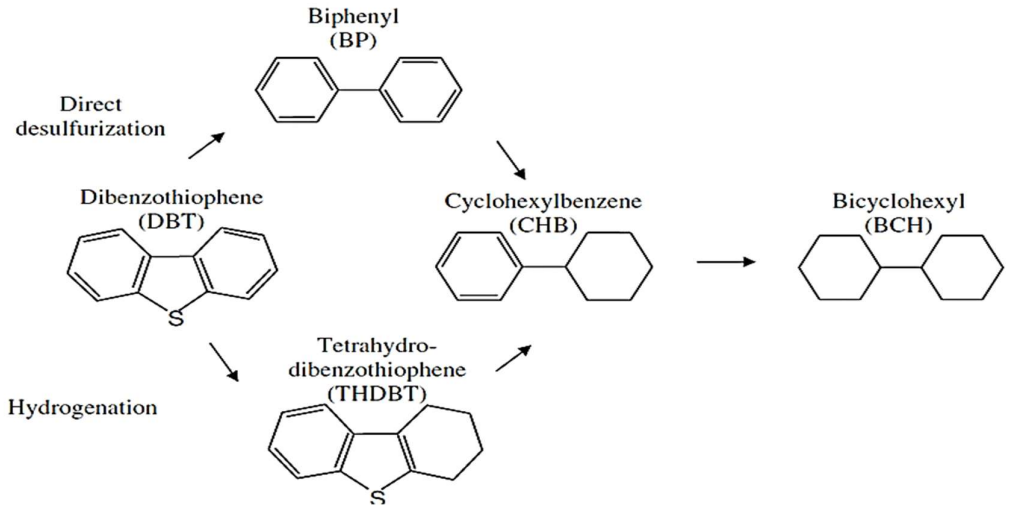


Fig 1.2 Mechanism of Hydrodesulfurization

The order of reactivity of various organosulfur compounds to HDS is:

Th > MTh > MBT > DBT > DMDBT

DMDBT, the least reactive sulfur in the HDS process, is significantly constrained in order to provide ultra-low level sulfur fuels, where more than 99% of sulfur compounds should be removed. The pace of desulfurization is slowed down as H2S accumulates on the catalyst's co-ordinately unsaturated surface throughout the process. Heterocyclic nitrogen compounds and aromatic hydrocarbons, which are found in fuels, both inhibit desulfurization. Reactor redesign will be necessary to achieve ultralow sulfur fuel, which means large, sophisticated, and maybe many more reactors. An improved, extremely active higher volume catalyst must be used. An improved catalyst with a higher, highly active volume must be used. Under extreme operating circumstances, such as high temperatures and hydrogen partial pressure, it is crucial to extract H2S from recycling gas.[13] The

technique becomes expensive when all of these requirements are combined, increasing the operational cost. The HDS Method of Desulfurization process is depicted in Fig. 1.3

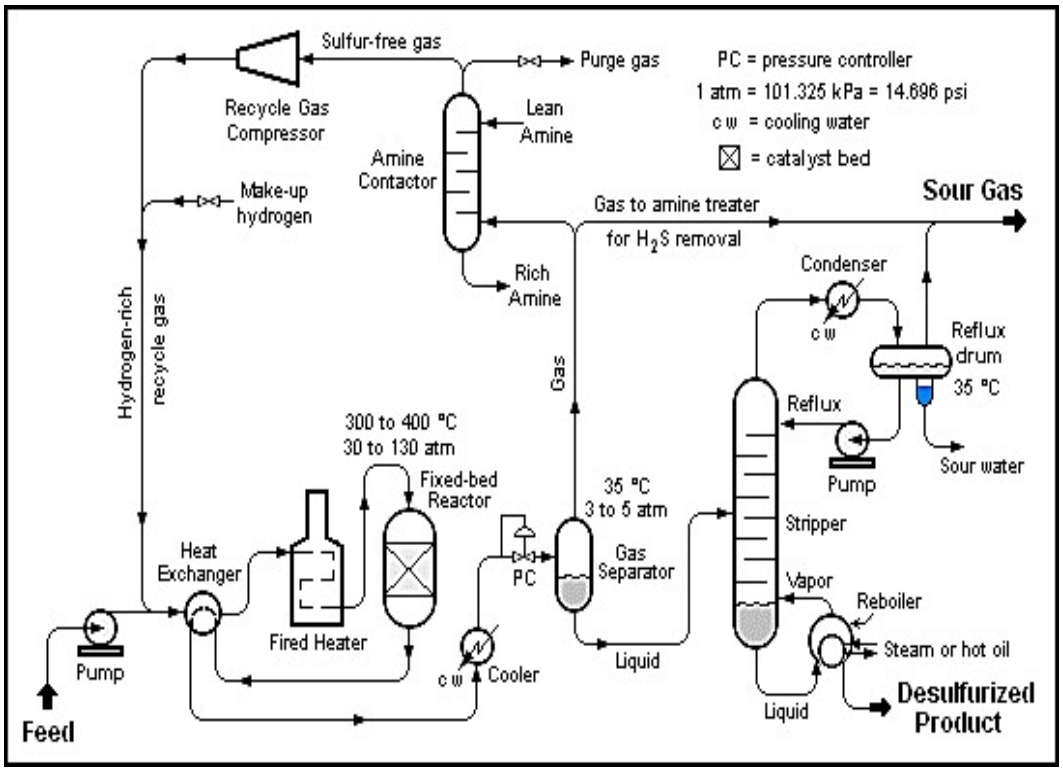


Fig 1.3 Schematic diagram for HDS process

1.3.2 Mechanism of Oxidative Desulfurization

Oxidative desulfurization (ODS) is a two-step process that converts organic sulfur compounds from petroleum fractions into polar sulfones and sulfoxides. The resulting sulfones and sulfoxides are then recovered using a polar solvent.[14] Unlike HDS, it operates at low temperatures and pressures, minimizing damage to hydrocarbon structures. The electron density of sulfur atoms directly affects the oxidation of sulfur compounds. The ODS is primarily a two-phase technique. The first stage involves oxidizing the target sulfur compounds. In the next step, these oxidized pollutants are extracted using a liquid extraction process. The ODS process entails oxidizing the sulfur compounds with the appropriate oxidants to turn them into the relevant sulfoxide and sulfones. Because of their

high relative polarity they are primarily extracted from light oils. Water washing and extraction can be used to remove any wasted oxidant that is still present in light oil. Fig 1.6 Represent the mechanism of ODS process.

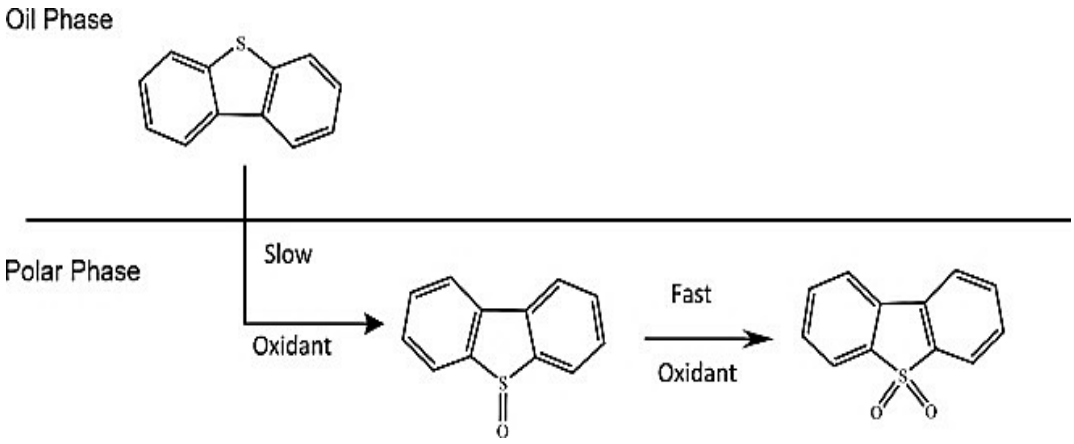


Fig 1.6 Mechanism of ODS process

1.3.4 Mechanism of Bio-Desulfurization

The 4-S process, which comprises the conversion of DBT (dibenzothiophene) into DBTO (dibenzothiophene sulfoxide), DBTO2 (dibenzothiophene sulfone), HPBS (2-hydroxyphenyl benzene sulfonate), and 2-HBP (2-Hydroxybiphenyl*),* is the most well-known mechanistic mechanism for the biodesulfurization of DBT. Fig. 1.4 shows the removal of sulfur in the form of sulfite. The "4s" pathway of enzymes, which are encoded by distinct genes, is depicted in Fig. 1.6. These enzymes include dibenzothiophene monooxygenase (DBT-MO or DszC), dibenzothiophene sulfone monooxygenase (DBTO2-MO or DszA), HPBS desulfinase, and NADH/FMN oxidoreductase. Among the common bacteria used in BDS are Arthrobacter, *Rhodococcus,* and *Pseudomonas.* Reaction factors like temperature and pH sensitivity have a significant impact on the process. This method is not suitable for industrial use because of the enzymatic reaction's intrinsic slow kinetics, which lead to a far slower rate of desulfurization than HDs, oxidative desulfurization, and adsorptive desulfurization. [15]

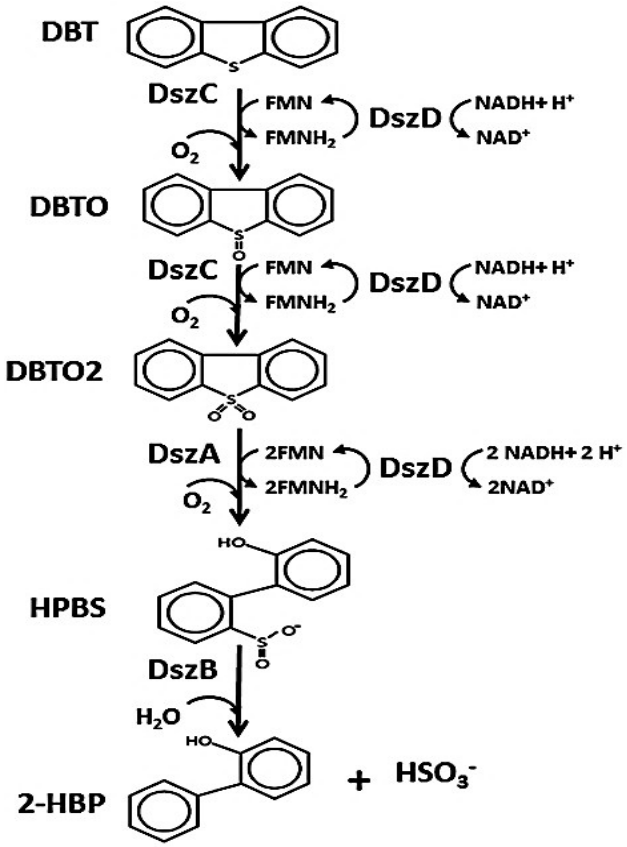


Fig 1.7 4-S pathway (sulfur specific) in Bio-desulfurization process

Dibenzothiophene (DBT) is one of the aromatic sulfur compounds that can be desulfurized by microorganism via the Kodama pathway. Prior to the now-famous 4S pathway, this was one of the earliest BDS pathways to be identified; however, it handled the sulfur atom differently. Fig 1.8 represents the mechanism of Kodama pathway

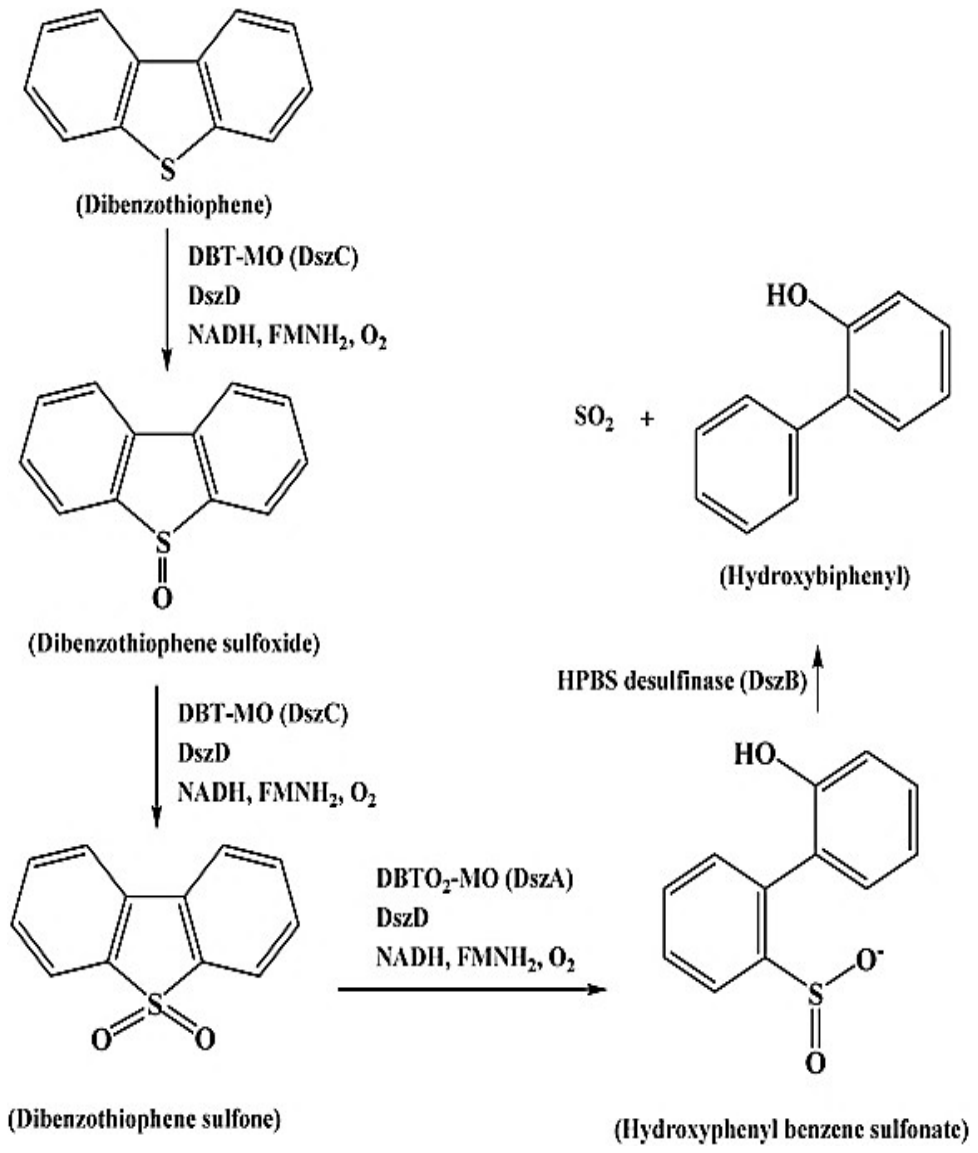


Fig 1.8 Kodama pathway Mechanism Pathway in BDS process

1.3.5 Mechanism of Extractive Desulfurization

A good solvent for extractive desulfurization should be inexpensive, nontoxic, have a high partition coefficient for aromatic sulfur compounds, be hardly soluble in fuels, and have high thermal and chemical stabilities. Conventional organic solvents like acetonitrile, N-methyl-2-pyrrolidone, dimethylsulfoxide, dimethylformamide, ethylene glycol, furfural, and polyethylene glycol were studied to remove sulfur compounds from petroleum

fractions. In EDS, extractants are used to extract the aromatic sulfur compounds from petroleum fractions at mild operating conditions without altering the chemical structure of compounds present in fuels. Due to similar polarities, a large percentage of aromatic hydrocarbons and organosulfur compounds are co-extracted, which results in a significant loss in fuel volume. Additionally, the experimental results demonstrated very low efficiencies of sulfur removal with these organic solvents.[16]

1.3.6 Mechanism of Adsorptive desulfurization

Adsorptive desulfurization (ADS) is one method that could be used to accomplish ultra-deep desulfurization. The ADS process has the potential to drastically lower sulfur levels when used in conjunction with HDS. ADS is a low-energy process that can be carried out at atmospheric temperature and pressure. It can be environmentally beneficial if bio-adsorbents are used. High sulfur specificity regenerable adsorbent materials could prove to be commercially feasible. These materials, which have been demonstrated to be efficient adsorbents, have been used to desulfurize metal organic frameworks, zeolites, activated carbon alumina, and zirconia refractory aromatic sulfur compounds. Adsorption is a surface phenomenon where molecules of adsorbate (gas, liquid, or dissolved solids) attach to the outermost layer of adsorbent materials (solid or liquid condensed phase) to produce a superficial layer. [17]

There are two types of adsorption process:

1.Physical adsorption

2.Reactive adsorption

1. Physical adsorption

A surface phenomenon known as physical adsorption, or physisorption, happens when molecules of a gas or liquid stick to the surface of a solid (referred to as the adsorbent) due to weak intermolecular forces, usually van der Waals forces. Because physisorption does not entail the creation of chemical bonds between the adsorbate and the surface, it is typically reversible and simpler to regulate than chemical adsorption, also known as chemisorption.

This process can happen with a variety of adsorbates, such as gases like nitrogen, oxygen, carbon dioxide, or compounds containing sulfur, and it typically takes place at low to moderate temperatures. In contrast to chemisorption, which is often restricted to a single layer, the adsorbed molecules can form several layers on the surface due to the low energy required (generally 20–40 kJ/mol). As adsorbents, materials with large surface area and porosity—like metal-organic frameworks (MOFs), silica gel, zeolites, and activated carbon—are frequently employed. Physisorption enables the selective removal of target molecules in processes such as gas purification, separation, or desulfurization. In order to regenerate the adsorbent, the process is frequently reversed by increasing the temperature or decreasing the pressure. Because physisorption is exothermic—higher temperatures tend to desorb the adsorbed molecules—it is best suited for low temperatures. It is significant in environmental and industrial processes due to its broad applicability, simplicity, and reversibility.[18]

2. Reactive adsorption

In the process of reactive adsorption, molecules (adsorbates) interact chemically with the adsorbent material in addition to being trapped on a solid surface. Reactive adsorption creates new chemical compounds on the surface as opposed to chemisorption, which includes surface bonding without changing the adsorbent, or physical adsorption, which depends on weak van der Waals forces. Reactive adsorption can be irreversible, meaning that the adsorbent gets "spent" and must be replaced or regenerated after saturation. It usually takes place at high temperatures to facilitate the process.[19] This method is frequently employed in environmental remediation, fuel refinement, gas purification, and

the elimination of trace poll

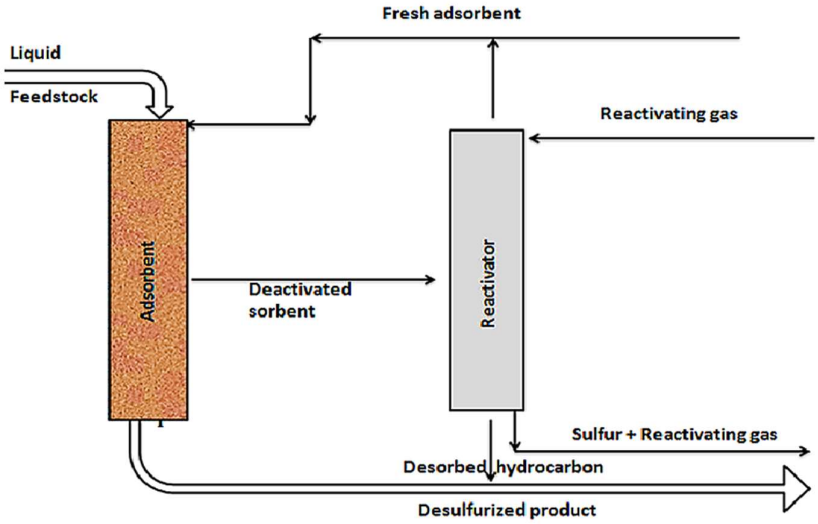


Fig 1.9 Adsorptive desulfurization unit

There are three types of mechanism in adsorption process:

1. Π- complexation
2. Direct S-M interaction
3. Hydrogen Bonding

1. **Π- complexation:** This kind of interaction occurs when electrons are donated from the d-orbitals of adsorbent metal atoms to the anti-bonding orbitals of organic sulfur compounds or transferred from the π π orbitals of organic sulfur compounds to the vacant s-orbitals of adsorbent metal atoms.

2. **Direct S-M interaction:** It entails the transfer of lone pair electrons from sulfur atoms of organic sulfur compounds to metal atoms of adsorbents, forming a direct sulfur metal σ bond.

3. **Hydrogen bonding:** The heteroatoms in sulfur-containing compounds, such as thiophenes, benzothiophenes, and dibenzothiophenes, have lone electron pairs that

can accept hydrogen bonds. A non-covalent contact between the sulfur molecule and the adsorbent occurs when the adsorbent surface or extracting solvent has functional groups (such -OH, -NH, or -NH_2 groups) that can donate hydrogen bonds.

1.4 Drawbacks of major Desulfurization technique

The most popular industrial process, hydrodesulfurization (HDS), uses a lot of energy and is expensive since it works at high temperatures (300–400°C) and high hydrogen pressures (30–130 atm). Furthermore, because to steric hindrance, it has trouble eliminating refractory sulfur compounds such as 4,6-dimethyldibenzothiophene. Efficiency is further decreased by catalyst deactivation over time due to coke production or metal poisoning, and ongoing hydrogen requirements raise operating expenses. Although bio-desulfurization (BDS) provides a gentle and eco-friendly substitute, its reaction rates are usually too slow for widespread use[21]. Process stability and scalability can be difficult due to the sensitivity of the microbial systems used in BDS to the fuel matrix, hazardous contaminants, or nutritional restrictions. Selective solvents are used in extractive desulfurization (EDS) to eliminate sulfur compounds; however, this process has limitations, such as high solvent costs, challenges with solvent regeneration, and a restricted capacity, particularly when non-sulfur chemicals are co-extracted. Solid materials like zeolites or activated carbon are used in adsorptive desulfurization, however their adsorption capability is sometimes restricted, particularly for large sulfur compounds. Selectivity can be weakened by competing adsorption of other hydrocarbons or nitrogen-containing compounds, and adsorbents can become saturated quickly and need to be often regenerated or replaced.[20]

1.5 Advantages of Adsorptive Desulfurization

As a potential substitute or addition to traditional sulfur removal techniques, adsorptive desulfurization has a number of benefits. One notable advantage is that, in comparison to hydrodesulfurization (HDS), it uses a lot less energy because it operates in mild circumstances, usually at ambient or slightly higher temperatures and pressures. Because it doesn't need hydrogen gas, it avoids the expense and hassle of managing and supplying hydrogen. When employing sophisticated adsorbents like metal-organic frameworks

(MOFs), zeolites, or modified activated carbons with specific pore diameters and surface functions, adsorptive desulfurization also demonstrates great selectivity for certain sulfur-containing molecules.[21]

Table 1.4 Types of Commercial Developed Adsorbents[22]

Adsorbent Type	Properties	uses
Activated Carbon	High surface area, microporous, regenerable	Adsorption of sulfur compounds, aromatics, impurities
Zeolites	Crystalline, uniform micropores, high stability	Selective adsorption of thiophenes, molecular sieving
Alumina (Al_2O_3)	High surface area, polar surface, acidic sites	Adsorption of polar sulfur species, moisture, metals
Silica Gel (SiO_2)	Amorphous, moderate surface area, hydrophilic	Adsorption of polar sulfur species, drying agents
Metal-Organic Frameworks (MOFs)	Ultra-high surface area, tunable pore size, functional groups	Selective adsorption of refractory sulfur compounds; emerging technologies
Clays & Pillared Clays	Layered structure, ion exchange capacity	Adsorption of sulfur species, often modified for selectivity

Table 1.5 Comparison of Biomass-Based Adsorbents[23]

Biomass Adsorbent Type	Source Material	Advantages	Limitations
Raw Biomass	Sawdust, rice husk, bagasse, coconut shell	Easily available, simple processing	Low surface area, limited adsorption capacity
Biochar	Pyrolyzed biomass (wood, straw, shells)	Good adsorption of organics and sulfur compounds, stable	Requires activation for best performance
Activated Carbon from Biomass	Activated biochar (via physical or chemical activation)	Excellent adsorption capacity, regenerable	Production cost, sensitive to competing species
Modified Biomass (functionalized)	Chemically treated biomass (with acids, bases, metals)	Improved selectivity and binding strength for target pollutants	Complex preparation, stability under conditions
Composite Biomass Adsorbents	Biomass mixed with clays, metal oxides, or polymers	Tailored adsorption behavior, multifunctional	More expensive, often harder to regenerate

Table 1.6 Different Metal Modification of *Euryale Ferox[23]*

Material	Modification	Target Sulfur Compounds (in Liquid Fuels)	References
Euryale ferox seed coat (activated carbon)	Physical/chemical activation (e.g., H_3PO_4, KOH)	Sulfur compounds like thiophene, benzothiophene (by analogy with other activated carbons)	Gupta, V. K., et al. (2011).
Euryale ferox husk activated carbon	Chemically modified (e.g., acid-functionalized)	Sulfur compounds, oxidized sulfur species	Wang, L., et al. (2020).
Euryale ferox–derived activated carbon	Metal-impregnated (Zn, Fe, Cu)	Thiophenic sulfur in liquid fuels	Kumar, P. S., et al. (2019).
Euryale ferox biochar	ZnO-modified	Thiophene, benzothiophene, dibenzothiophene	Christian Frilund* Pekka Simell (2020)
Euryale ferox biochar	Fe_3O_4-modified Cu^{2+}-modified	Thiophene, dibenzothiophene	Bowen Yang [a], Jiawei Dai [b]
Euryale ferox biochar	Bi_2MoO_6-modified CaS-modified	Sulfur compounds, heavy metals	Ming-shan Xue (2022)

1.6 Titanium Metal for Modification of Activated Carbons

Titanium is one of the best modifiers for adsorptive desulfurization due to its strong chemical affinity for sulfur compounds and its excellent stability. In the form of TiO_2 or titanium ions (Ti^{4+}), it acts as a strong Lewis acid, which allows it to interact effectively with sulfur-containing molecules like thiophene and dibenzothiophene. These interactions enhance the selective adsorption of sulfur over hydrocarbons.

Titanium-modified adsorbents also exhibit improved surface properties, such as increased surface area, pore volume, and active sites. These properties are essential for capturing sulfur molecules efficiently. Additionally, titanium forms stable Ti–O–C bonds when combined with porous carbon supports (such as biomass-derived materials), enhancing durability and electron transfer at the surface.

1.7 Aims and Objectives

The current thesis's goals are as follows:

- The primary aim of this study is to develop and evaluate a green, efficient, and reusable adsorbent for sulfur removal from liquid fuels. The specific objectives include:
- Synthesizing activated carbon from Euryale ferox shell waste, a readily available but underutilized agricultural by-product.
- Modifying the synthesized carbon with titanium to improve its sulfur adsorption efficiency.
- Investigating adsorption behavior, including kinetics, isotherms, and thermodynamics, using both model sulfur compounds and real fuel samples.
- Assessing the regeneration potential and long-term usability of the Ti-modified adsorbent across multiple cycles.
- This work aims to deliver an eco-friendly and cost-effective alternative to conventional desulfurization technologies while promoting biomass valorization and environmental sustainability.

CHAPTER 2:

MATERIALS AND CHARATERIZATIONS

Chapter 2: Material and Synthesis

2.1Materials

2.1.1Some sulfur-containing compounds in liquid fuels

Dibenzothiophene (DBT)

For the current study, DBT (Assay:98) was obtained from Sigma-Aldrich (CAS No: 132-65-0). The DBT has a molecular weight of 184.26 g/mol and the empirical formula $C_{12}H_8S$. The compound has a melting point of 97-100 degrees Celsius and a boiling point of 332-333 degrees Celsius. DBT is a naturally occurring component of diesel. The compound's chemical structure is given in Fig 2.1

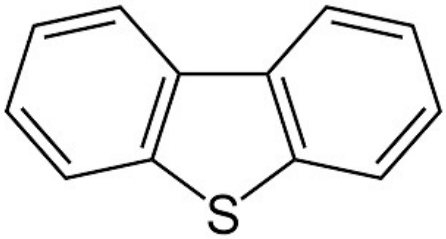


Fig. 2.1 Chemical structure of DBT

2.1.2 Solvents

The model oil can be made with a variety of solvents, such as hexane, cyclohexane, octane, and heptane. Because it was colourless, reasonably priced, and simpler to analyze using gas chromatography, iso-octance was used as a solvent in the model oil formulation. It was acquired in HPLC grade from RANKEM. The molecular weight of iso-octane is 114.23g/mol, and its chemical formula is C_8H_{18}. The assay value and specific gravity were found to be 99% and 0.69, respectively.

2.1.3 Activated Carbons

A highly porous carbonaceous substance, activated carbon (AC) is a great adsorbent for industrial and environmental applications due to its high porosity, huge surface area (500–2000 m^2/g), and adaptable surface chemistry. It is generally made using two primary techniques: chemical activation, in which raw materials are impregnated with activating agents such as potassium hydroxide or phosphoric acid and then heated, and physical activation, in which carbon-rich materials are carbonized at high temperatures and then activated with steam or CO_2. Surface processes involving oxygen-containing functional groups on the AC surface, π–π interactions between the aromatic rings of sulfur compounds and the graphitic carbon surface, and physical adsorption via van der Waals forces are the main adsorption mechanisms on AC. Unmodified activated carbon, on the other hand, usually exhibits modest sulfur removal efficiency. Low selectivity for sulfur compounds, saturation at low adsorption capacities, and competition with other fuel-derived hydrocarbons are the main causes of the limits. The nanopores range in size from 2 to 100 nm. According on pore size, dimension nanopores can be divided into three categories: micro, mesoporous and macroporous. The size of micropores is 2 nm. Activated carbon may be a good adsorbent because of its large specific surface area, porosity, and variable surface chemistry. Because adsorbents can withstand changes in temperature as well as acidic and basic desorption solutions, regeneration is feasible [41]. Regeneration is possible because physical adsorption is a reversible process. Adsorbent can therefore be utilized again as an adsorbent. [24]

2.1.4 Carbon Based Materials

A diverse class of adsorbents and catalysts, carbon-based materials are frequently employed in environmental applications, such as the extraction of sulfur from liquid fuels. Activated carbon (AC), carbon nanotubes (CNTs), graphene, mesoporous carbon, carbon black, and biochar are important examples.[25] These materials are prized for their customizable surface chemistry, high surface area, porosity, and chemical stability. They target substances that are challenging to remove using traditional techniques, such as thiophene, benzothiophene (BT), and dibenzothiophene (DBT), in order to remove sulfur. With removal rates of up to 80–98%, performance can be greatly improved by employing

metal-impregnated carbons (using Zn, Fe, Cu, etc.), nitrogen-doped carbons, or mesoporous carbons. Excellent sulfur adsorption is also demonstrated by CNTs and graphene because of their well-defined structures and tuneable surfaces, particularly when functionalized or metal-loaded. All things considered, carbon-based materials are essential to the production of clean fuel and environmental remediation because they provide an affordable, scalable, and highly adjustable foundation for cutting-edge desulfurization methods.

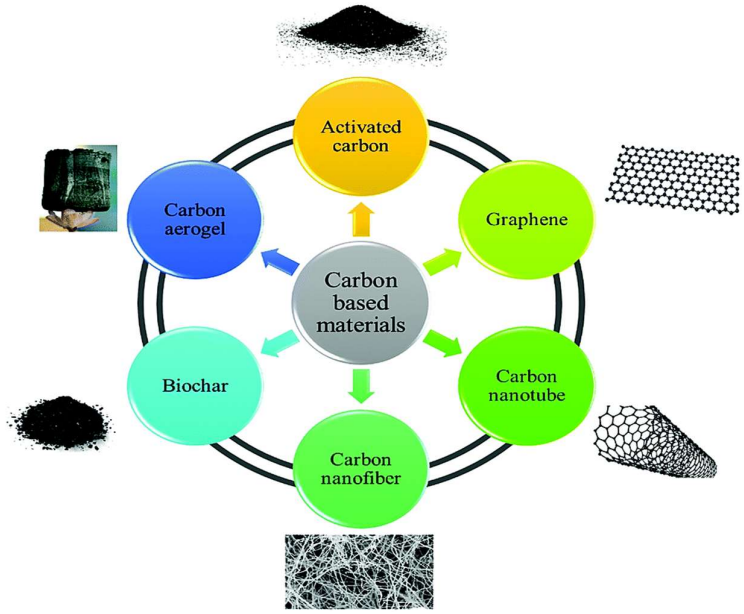


Fig 2.2 Carbon-Based Materials

2.1.5 Chemicals used for preparation of FAT and Ti@FAT

Liquor ammonia

Liquor ammonia (25%) was used as a reducing agent for the formation of Ti@FAT. It had a molecular weight of 17.03 g.mol-1. It was procured from fischer scientific (CAS No: 1336-21-6) and has specific gravity 0.91.

Ethylene Glycol

Ethylene glycol act as a binding agent for the formation of Ti@FAT. Its molecular weight is 62.07 g/mol. Its specific gravity at room temperature is 1.13.

2.1.6 Lab Equipment Used

The muffled furnace (THERELEK, India), ultrasonic bath cleaner (Ultrasonicator FS4), gas chromatography, and orbital shaker (EIE Instruments, India) were used in the current experiments. Gas chromatography used for sulfur analysis in model oil. Muffled furnace used in synthesis of FAT and Ti@FAT by removing impurities. Sonicator is used in fabrication of carbon surface.

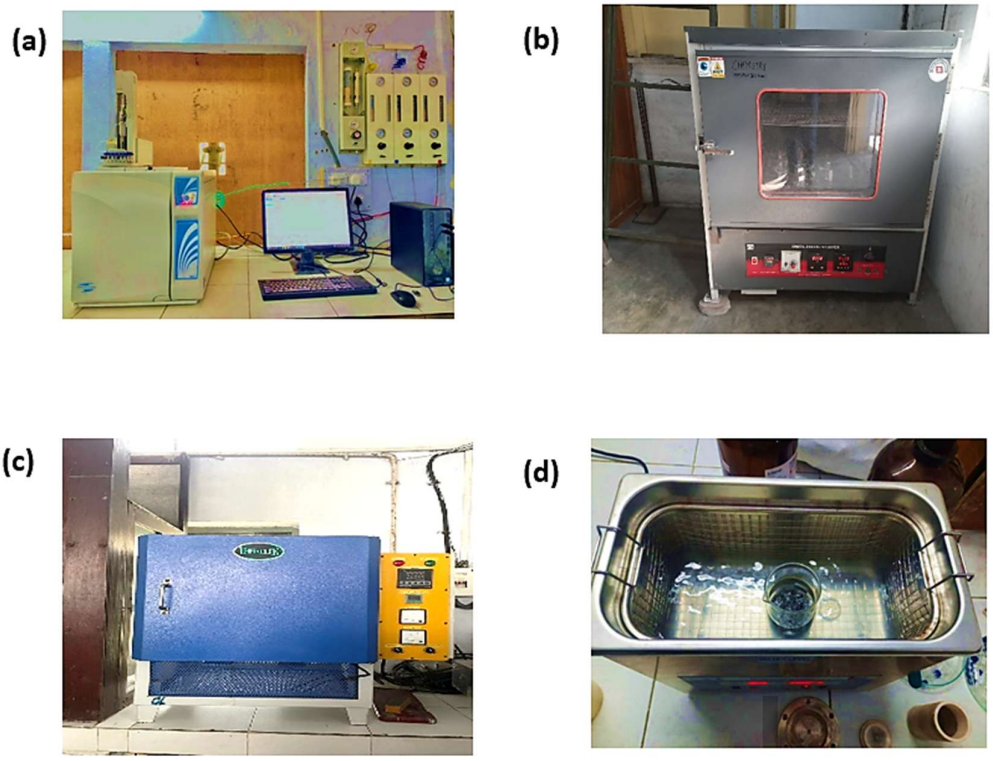


Fig2.3 a) Gas chromatography b) Orbital shaker c) Muffled furnace d) Sonicator

2.2 Information on Euryale Ferox Source for Activated Carbon

Euryale ferox, has a spiny seed covering (thrones and shells) that are typically discarded during processing. However, recent studies and sustainable material research have found that these waste by-products can be converted into activated carbon. The thrones and seed shells of Euryale ferox are rich in carbonaceous material. These are typically considered agriculture waste, making them a low-cost, eco-friendly source for activated carbon production.

2.2.1 Synthesis of *Euryale ferox* Activated Carbon

The schematic illustration of the synthesis of FAT is shown in Figure 2.4. After being bought from a local shop near the VNIT in Nagpur, the *Euryale Ferox* shells were meticulously scraped and crushed, cleaned with distilled water, and allowed to dry in the sun. For one hour at 50 degrees Celsius, orthophosphoric acid (1:1 w/v) was used to further activate the powdered *Euryale Ferox* shell. After that, the sample was heated in a tube furnace to 550 C at a rate of 10 C/min while air was present, and it was then kept at that temperature for 1 hour in a muffle furnace.

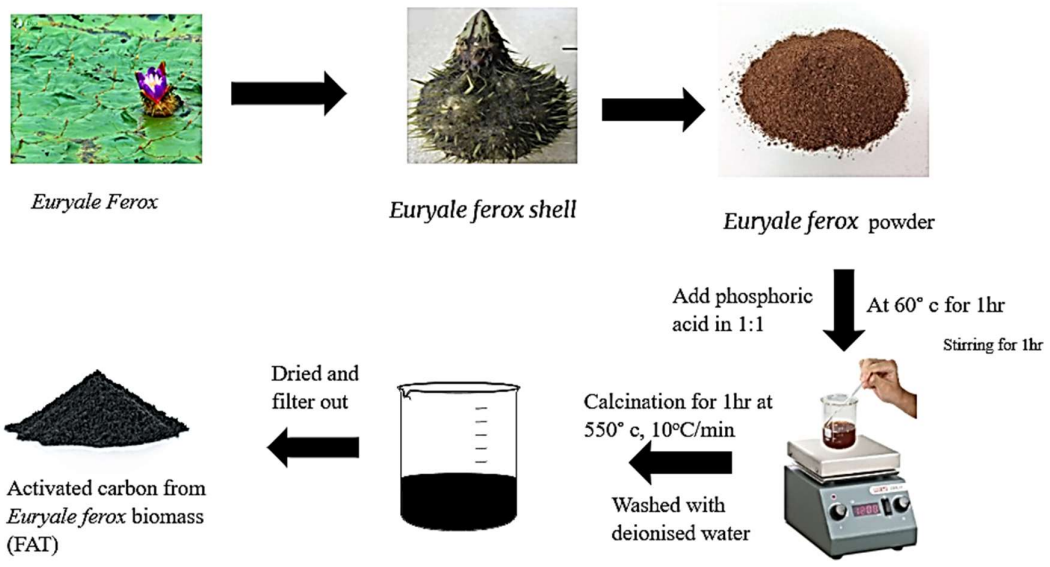

Euryale Ferox
Euryale ferox shell
Euryale ferox powder
Add phosphoric acid in 1:1
At 60° c for 1hr
Stirring for 1hr
Calcination for 1hr at 550° c, 10°C/min
Washed with deionised water
Dried and filter out
Activated carbon from Euryale ferox biomass (FAT)

Fig. 2.4 Steps involved in the synthesis of FAT

2.4 Synthesis of Titanium modified activated carbon (Ti@FAT)

In a 500 mL beaker, 100 mL water, 50 mL ethanol, and 5 g of FAT were combined and agitated at room temperature. After 1.5 hours, 10 mL of 1.0 M NaOH (aq), 15 mL of NH_4OH and 15 mL of ethylene glycol were added dropwise. The ethylene glycol served as a binding agent. Titanium Tetrachloride salt is added to this mixture after 5minutes. For 6 hours, the resultant mixture was continually swirled at 50 °C. The resulting carbon was filtered out by whatman filter paper. The powder was dried overnight in an oven at 85 °C before being calcined for 4 hours at 350 °C in a silica crucible; finally, Ti-impregnated carbon was obtained and is known as Ti@FAT. Fig. 2.5 steps involved in the synthesis of Ti@FAT.

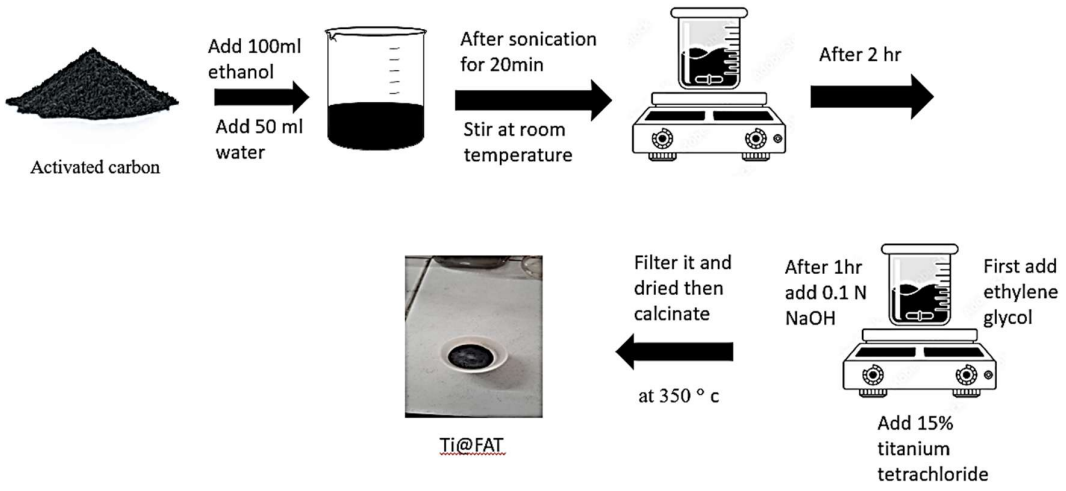


Fig. 2.5 Steps involved in the synthesis of Ti@FAT

2.4 Preparation of Model Fuel

To prepare 200 ppm of S-containing model oil, we have used iso-octane as solvent medium, and for sulfur DBT has used because it organosulfur compounds. DBT was mixed with solvent and solution and stirred well. Prepared 200 ppm model oil in 500ml. The concentration of DBT in model fuel and desulfurized model fuel was determined using

equation y= mx + c, and calibration study was done using concentrations of 200, 100, 50, 25 and 12.5ppm of model oil through gas chromatography equipped with flame photometric detector (GC-FPD) for DBT in iso-octane. Fig. shows the calibration curve of DBT in GC.

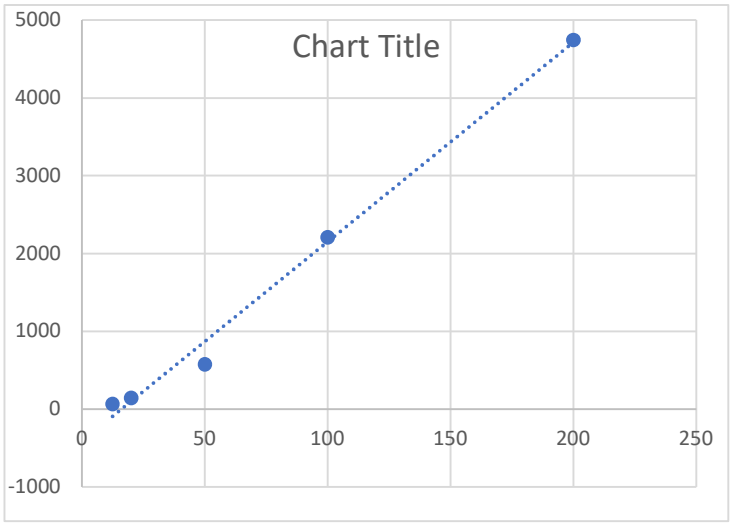


Fig 2.6 calibration curve for DBT

2.5 Preparation of Multicomponent Simulated Model Fuel

We used to prepare simulated model fuel by using Hydrogen fraction such as iso-octane and sulfur fraction (ppm) such as thiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene. The initial concentration is 53 ppm, 115.2 ppm and 213.1 ppm of Thiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene. The initial and remaining sulfur concentrations in multicomponent simulated model fuel were measured using GC-FPD. Also, the initial and treated sulfur concentrations in kerosene fuel were measured by using GC-FPD The retention times of selected sulfur compounds present in MSMF and kerosene were calibrated using appropriate standards of TH, DBT, and 4,6 DMDBT. GC-FPD chromatogram was used to analyse the initial and final concentrations of Ti@FAT. GC chromatograms indicated significant peaks corresponding to TH, DBT, and 4, 6-DMDBT at retention times 3 min, 8.1 min, and 9.3 min, respectively.

2.6 Plausible Interaction of Titanium metal centres with sulfur atom

In the present work, Titanium (Ti) has garnered significant interest for the modification of activated carbons in sulfur removal applications due to its unique chemical and structural properties.[26]

1. High Affinity for Sulfur Compounds

Titanium exhibits a strong chemical affinity for sulfur, forming stable titanium-sulfur (Ti–S) bonds. This interaction enhances the capture of sulfur-containing molecules such as thiophene, benzothiophene (BT), and dibenzothiophene (DBT), which are commonly found in liquid fuels.

2. Lewis Acid–Base Interactions

Titanium ions (especially Ti^{4+}) act as strong Lewis-acids that interact with sulfur atoms, which serve as soft Lewis bases. This acid-base interaction facilitates the selective binding of organosulfur compounds on the surface of titanium-modified adsorbents

3. Surface Functionalization and Increased Active Sites

Ti-impregnation can alter the surface chemistry of activated carbon by introducing new functional groups and enhancing surface polarity, which improves the adsorption of polar sulfur species. we have chosen Ti for modification of activated carbon because of its significant chemical affinity for sulfur, titanium metal is thought to be very effective for desulfurization. Easily forming stable sulfides (like TiS and TiS_2) as a reactive transition metal, titanium aids in the effective uptake and binding of sulfur atoms from a variety of environments. Due to its high reactivity and function as a hard Lewis acid, titanium can interact with sulfur, a softer Lewis base, under the right circumstances, forming this strong Ti–S bond. Additionally, titanium performs exceptionally well at high temperatures, which are frequently needed for desulfurization procedures, particularly in metallurgy and refinery. Durability and lifespan in desulfurization systems are guaranteed by its resistance to corrosion and capacity to tolerate hostile chemical conditions. Furthermore, titanium is especially well-suited for catalytic or direct sulfur removal procedures due to its surface

characteristics, which include its capacity to provide active sites for sulfur adsorption and reaction. There are two types of interactions that can occur, as outlined below:

2.7 Characterization Techniques

2.7.1 Powder X-ray Characterization

Phase analysis with powder X-ray diffraction (XRD) provides information about the crystal structure, interplanar distance and lattice parameters of solid powder samples. In this technique, the sample is exposed to an X-ray beam and diffraction patterns with varying angles of incidence recorded.[27] Both angle and pattern are determined by the diffracted strength. The whole assembly is comprised of an X-ray source with wavelength ranging from 0.7 to 2 A^o, collimators and the detector. X-ray diffraction is based on the Bragg's equation which can be explained as follows:

$n \lambda = 2d \sin \theta$……. (2.1)

where, n = order of diffraction (1,2,3, …), λ = wavelength of X-ray, d = interplanar distance between crystalline planes, θ = angle of incidence of X-ray

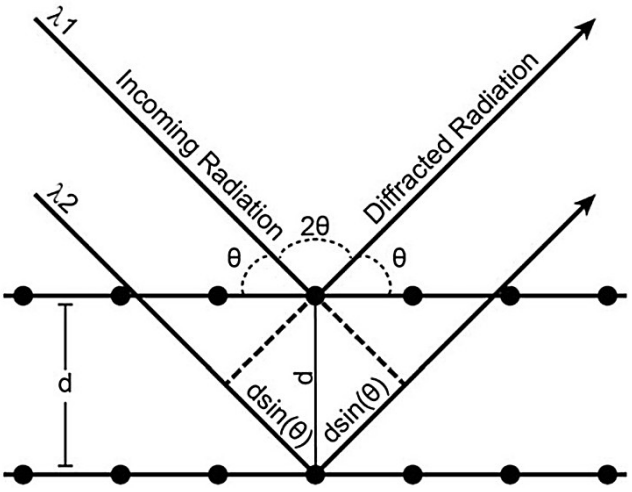


Figure 2.6 Representation of Bragg's diffraction in crystal structure

A plot of diffracted ray intensity versus diffraction angle 2 θ gives a unique pattern, with a corresponding set of planes. The most important application of Scherrer's equation is in

X-ray diffraction (XRD), which uses the broadening of diffraction peaks to estimate a material's crystallite size.

The Scherrer's equation (eq 2.2) can be explained as follows:

$D = K\lambda / \beta \cos\theta$……. (2.2)

(where, D is the crystallite size in A^o, K = 0.9 is Scherrer's constant, λ is the wavelength of X-ray in A^o, β is the full width at half maximum (FWHM) of the peak (in radians), θ = incident angle or Bragg's angle.

2.7.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is an advanced technique used to determine the presence of various functional groups present in the sample. FT-IR measures a material's absorption of infrared light at different wavelengths to produce an infrared spectrum of that material. Unlike IR spectroscopy, FT-IR uses an interferometer to gather all wavelength data simultaneously. The raw signal so obtained is then transformed into a readable spectrum using a Fourier transform. This technique helps to identify functional groups, chemical bonds, and material composition in solids, by enabling a higher resolution, quicker and more precise determination of molecular vibrations. An FT-IR spectrum normally covers the mid infrared region, which is particularly important for identifying chemical vibrations and functional groups, between 4000 and 400 cm^{-1}. The fingerprint area (1500 – 400 cm^{-1}) which contains complex absorption patterns particular to each molecule, and the functional group region (4000 – 1500 cm^{-1}) where the presence of strong peaks identify particular bond types like O-H, N-H, and C=O are two important absorption zones included in this range. Because of its wide spectrum range, FT-IR provides structural details on both organic and inorganic compounds.[28]

2.7.3 Surface area and pore size distribution

Surface area and porosity are important characteristics in the field of catalysis design and heterogeneous catalysis. Since total surface area affects accessibility to the active site and

is thus frequently linked to catalytic activity, it is a crucial component of solid catalyst performance. The Bruner-Emmett-Teller (BET) technique theory can be applied to nitrogen adsorption isotherms to determine the surface area and pore size of powder and porous materials. The degree of gas adsorption rises with increasing pressure and is proportional to the relative pressure. The BET analysis makes the assumption that adsorption takes place on a free surface at saturation pressure and that is accomplished by creating multiple adsorbed layers with an infinite number of adsorbed layers. The Langmuir adsorption isotherm is the model that corresponds to the maximum adsorption and is represented by monolayer adsorption. [29]

$C_e/ q_e = 1/ q_{max} K_L + C_e/ q_{max}$……. (2.3)

Where, q_e = amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g)

C_e = equilibrium concentration of adsorbate in solution (mg/L)

K_L = Langmuir constant related to the affinity of binding sites (L/mg)

To determine the surface area and pore size of the catalyst, Qunatachrome Nova touch 1 BET surface area analyzer was used.

2.7.4 Scanning Electron Microscope (SEM)

SEM (Scanning Electron Microscope) is an advanced imaging technique that uses a focused beam of high-energy electrons to generate signals from the surface of solid specimens. These signals are used to form high-resolution, three-dimensional-like images of the surface. SEM is used to Examine surface morphology and topography in great detail. Analyze particle size, shape, and distribution. Investigate elemental composition using EDX/EDS (Energy Dispersive X-ray Spectroscopy). Study fracture surfaces, microstructures, and coatings. Observe adsorption mechanisms on catalyst or adsorbent surfaces. [29]

2.8 Determination of Sulfur Content in Liquid Fuels

1. GC-FPD

Gas chromatography with a flame Photometric Detector (GC-FPD), image shown in Fig 2.7 which detects chemiluminescent elements such as sulfur, phosphorous, arsenic, and so on Furnace: R-S+ O_2 H_2 + SO_2 + By products

$SO_2 + H_2 + SO + H_2O$

Reaction Cell: SO + O_3 SO_2 *+O_2

SO_2 * SO_2 + UV light

The amount of SO_2 gas produced is proportional to quantity of Sulfur compounds present in the fuel. The sulfur samples sample has been run by GC-FPD program by developing a method as describe below. Unknown concentrations were determined using a GC-FPD of Chromatec- Crystal 9000 on a GS BP-1 capillary column (30 m × 0.32 mm × 4 m) using Helium as the carrier gas at a capillary flow rate of 3 mL min^{-1}, continuous hydrogen flow (140 mL min^{-1}), and airflow (40 mL min^{-1}). The oven temperature of FPD was 250 °C with a sample injection volume of 0.1 µL and a total analysis time of 10 min with a 0.9 min hold period.[30]

Fig 2.7 GC-FPD Chromatogram

2. UV- Spectrophotometer

Thiophene, Benzothiophene, and Dibenzothiophene all absorb at a different wavelength that is determined by their molecule as well as the solvent environment. These compounds found to have maximal absorption wavelengths in the UV range, namely 325 nm for dibenzothiophene & 232 nm for thiophene in Iso-Octane as a solvent. The relationship between absorbance and sulfur compound concentration can be expressed as follows. Absorbance is directly proportional to the Concentration. It also indicates on the adsorbent's surface, and so the adsorbent's capacity may be determined. As a result, it is an indirect means of determining the extent the adsorption. Figure 4.6 depicts a typical UV-VIS spectrometer used for measurement[31].

Fig. 2.8 UV- Vis Spectrophotometer

CHAPTER 3:

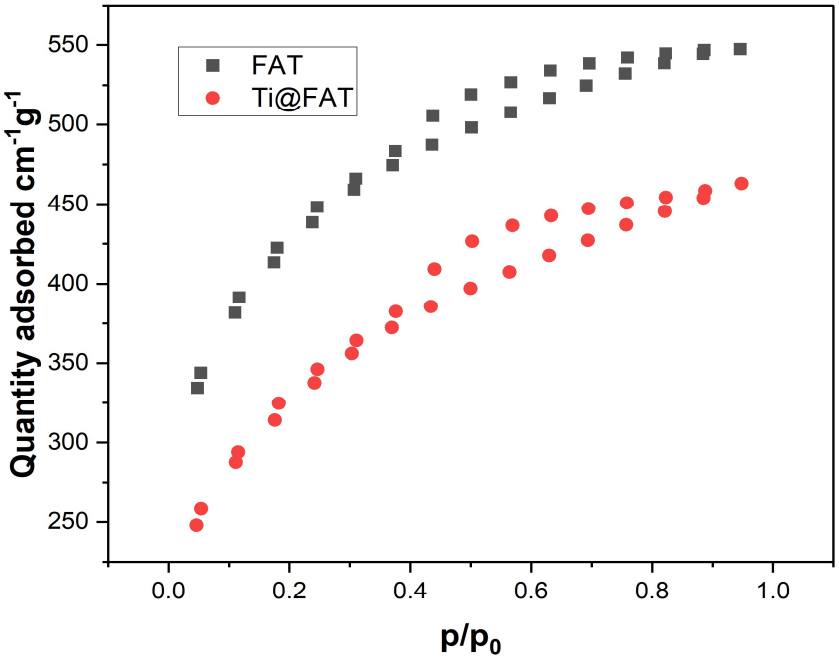
RESULTS AND DISCUSSION

3.1 Characterization

3.1.1 BET Surface Area Analysis

Target chemical removal through adsorption is greatly aided by the porous structure and surface characteristics of activated carbon [32]. To learn more about the surface nature and texture of the created materials, the BET surface area analysis and the BJH model for pore size distribution were investigated. The BET isotherm for nitrogen adsorption and desorption at the carbon surface was determined at a fixed temperature of 77.3 K. Before analysis, the material was degassed for 24 hours at 80^0C. The plot's hysteresis loop indicates that mesoporous and macroporous structures are present on the surfaces of FAT and Ti@FAT. FAT and Ti@FAT were found to have surface areas of 1400 m^2g^{-1}, 1095 m^2 g^{-1} respectively.

(a)



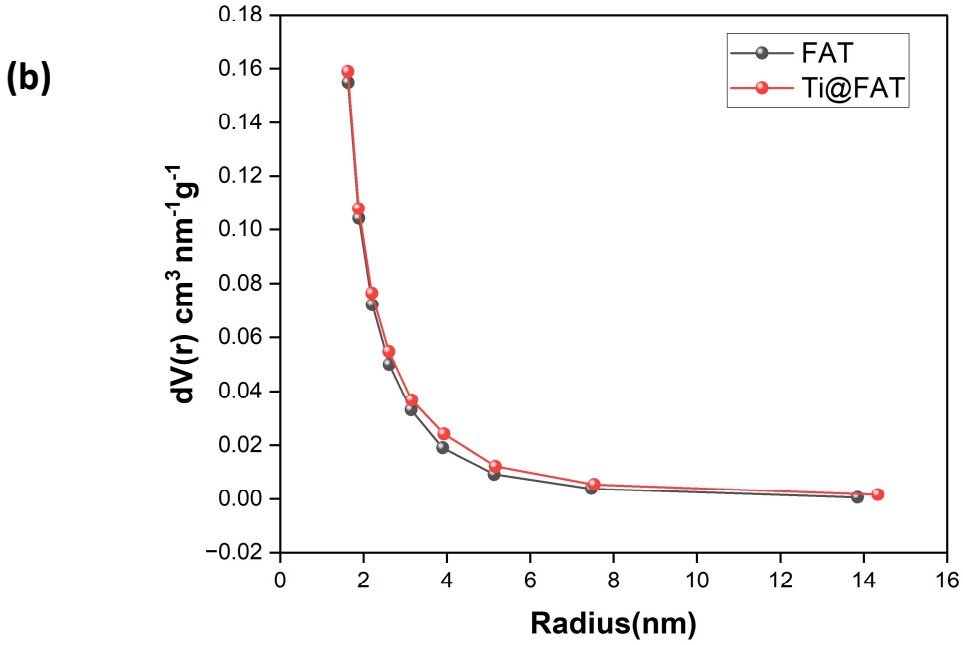


Fig. 3.1 Nitrogen adsorption -desorption curve of FAT and Ti@FAT

Table 3.1: Surface area and porosity details of FAT and Ti@FAT

Adsorbents	Surface Area m^2/g	Pore Volume cc/g	Pore Radius nm
FAT	1400	0.183	1.63
Ti@FAT	1095	0.218	1.63

3.1.2 FTIR Analysis

The FT-IR analyzer (Shimadzu, India) was used to record the FT-IR spectra of the developed materials. The spectra were collected in the 4000-400cm^{-1} wavelength range.

The FT-IR spectra shown in Fig. 3.2 can be used to understand the typical vibrational frequencies for the various functional groups of the materials.

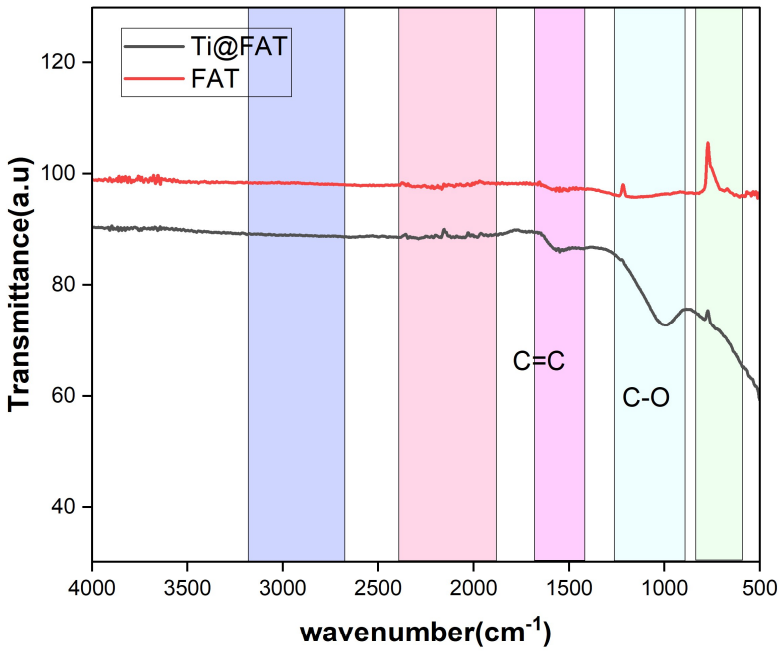


Fig 3.2 FT-IR Spectra of FAT and Ti@FAT

A peak around 1000-1200 cm^{-1} suggests the presence of C-O bonds, possibly indicating alcohols, ethers, or carboxylic acids. Peaks around 1600 cm^{-1} indicate the presence of C=C bonds, which could be due to the presence of aromatic or unsaturated compounds. The Ti@FAT spectrum shows some differences compared to the FAT spectrum, particularly in the intensity and position of the peaks. This suggests that the addition of titanium has altered the chemical environment and functional groups present in the material. The changes in the Ti@FAT spectrum may indicate the interaction between titanium and the functional groups of FAT, leading to the formation of new bonds or changes in the existing ones. In case of Ti@FAT more functional group is present compare FAT means functionality of FAT increases after the modification by Titanium.

3.1.3 PXRD Analysis

Fig 3.3 represents the X-ray powder diffraction spectra of FAT and Ti@FAT. In case of FAT bump peak is more compare to Ti@FAT, this is show that amorphous nature of FAT and slightly crystalline nature of Ti@FAT after modification with Titanium and peaks are matching with JCPDS file No. 96-512-0783

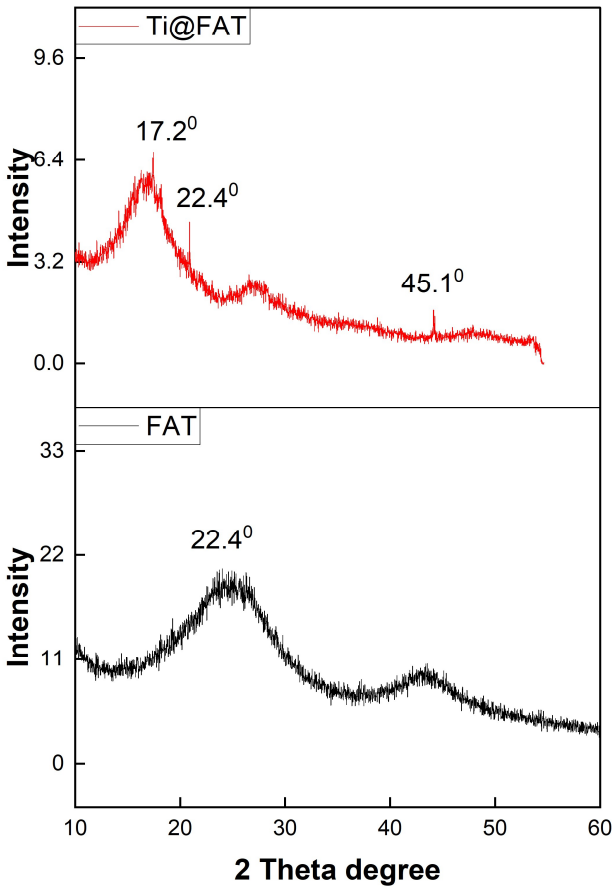


Fig. 3.3: PXRD spectra of FAT and Ti@FAT

3.1.4 TGA Analysis

Thermo-gravimetric analysis curve of Ti@FAT and FAT (Fig3.4) whereby with the increase in temperature, three primary steps in mass loss are seen shows. The weight loss analysis showed three distinct peaks. The initial loss, occurring at approximately 100 °C,

indicated the evaporation of adsorbed moisture. The second and most significant loss occurred in the temperature range of 480°C, which corresponded to the breakdown of hemicelluloses and organic matter. The third peak, observed between 560°C, was due to the decomposition of lignin and cellulose. At 600^0C FAT weight loss is 23% and Ti@FAT weight loss is 3% It shows thermal stability of Ti@FAT is greater than FAT.

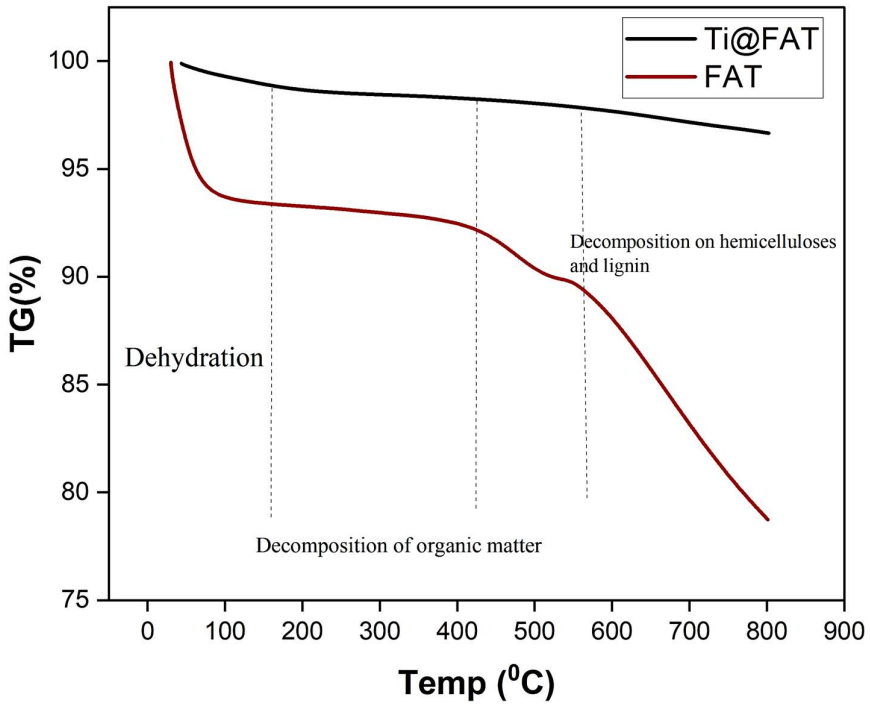


Fig. 3.4: TGA curve of FAT and Ti@FAT

3.2 SEM Analysis

The images show a SEM micrograph of Titanium-Loaded Euryale Ferox nanoparticles. The SEM images revel the morphology and size of the synthesized nanoparticles. Several particles are measured and labelled in the images, showing sizes ranging 36.2 nm to 51.0 nm. The scale bar indicates that 100 nm is represented by the length shown, and the magnification is X 100,000. The accelerating voltage used for imaging is 5.0 kv, and the working distance is 14.0 mm. the particles appear to be relatively uniform in size, mostly

falling within the range indicated by measurements. The distribution seems fairly even across the field of view. The images appear somewhat spherical or irregular, with a granular texture. They seem to be agglomerated, forming clusters rather than existing as individual, well-dispersed particles. EDS images show that presence of Carbon, Oxygen and titanium in the sample. The graph shows the intensity of X-Ray emitted by each element, allowing for the determining of their weight percentages. The most abundant element, Carbon with a weight percentage of 82.8%. this is expected as Euryale ferox is primarily composed of organic matter. Oxygen with 16.7% weight this is expected as Euryale ferox is primarily composed of organic matter. Titanium with a weight of 0.5% this indicates the loading of titanium onto the Euryale Ferox. The surface morphology of FAT is uneven and rough, featuring numerous pores and cavities. This type of structure can affect the material's surface area and adsorption properties. EDS morphology of FAT is Carbon with 77.7% weight and oxygen with 22.2%.

(a)

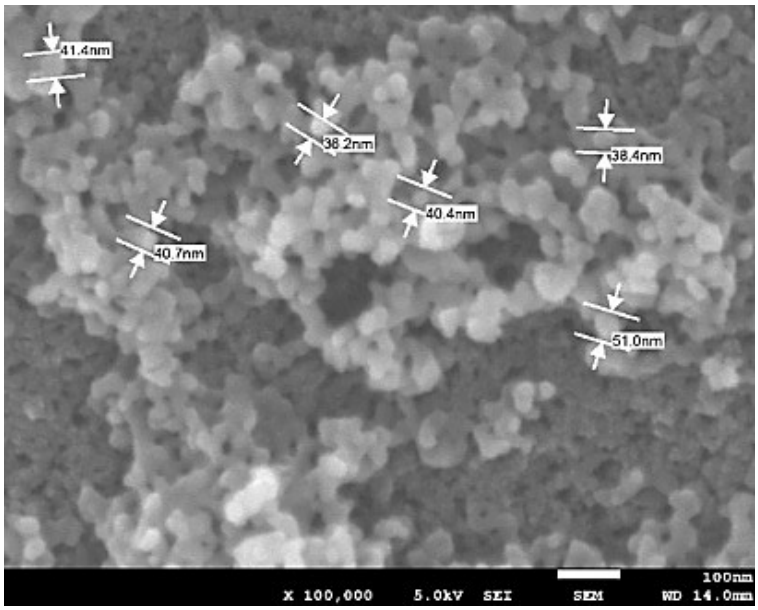


Fig 3.5 SEM Analysis for FAT

(b)

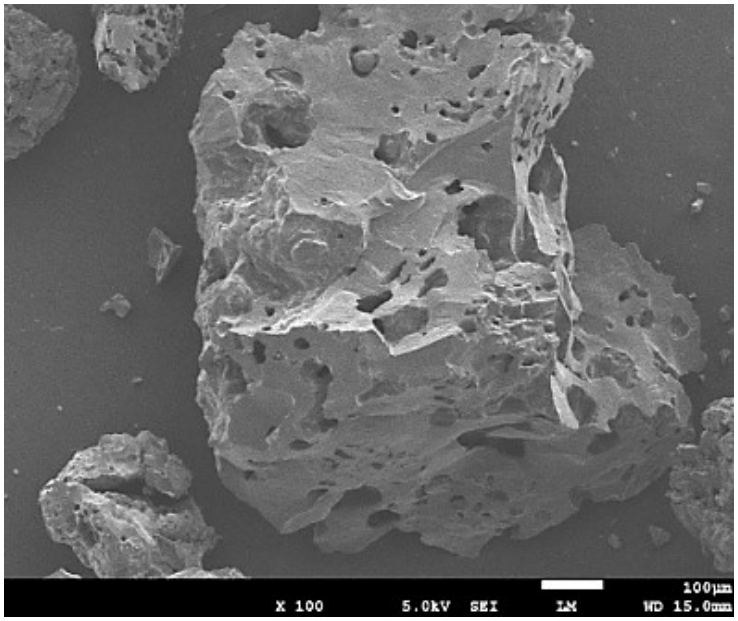


Fig 3.6 SEM Analysis for Ti@FAT

(a)

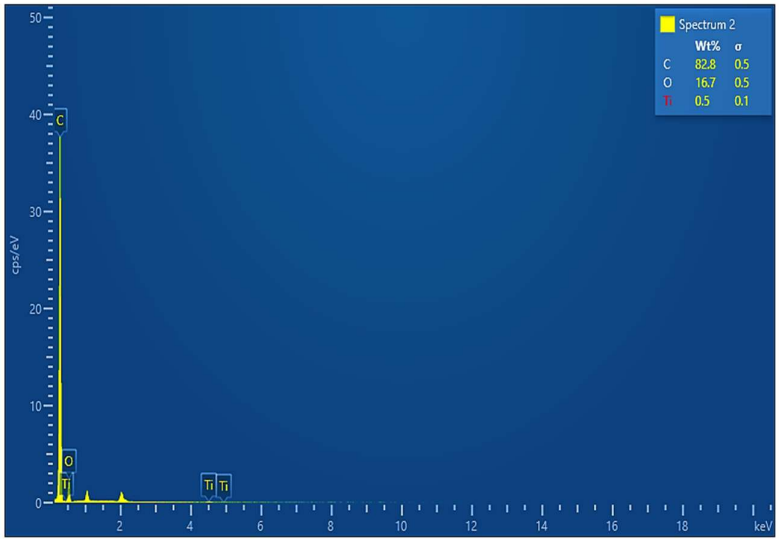


Fig 3.7 EDS analysis of Ti@FAT

(b)

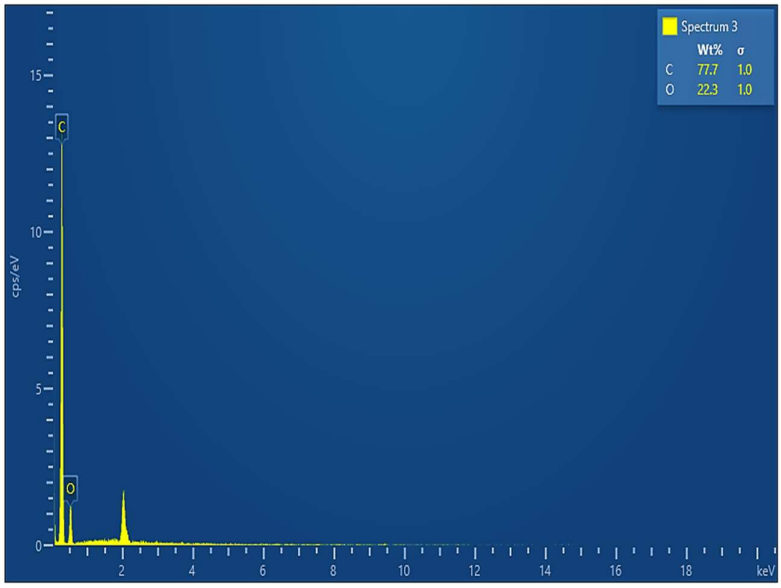


Fig3.8 EDS analysis for FAT

3.3 Effect of Adsorbent Dosage

The dose was optimised by introducing different adsorbent dosages of FAT and Ti@FAT ranging from 0.01 to 0.10g into ml of model oil (200 ppm DBT in iso-octane) ml in Erlenmeyer flasks. These flasks were then placed in an orbital shaker at 30^0C for 3 hours at 100 revolutions per minute. The flasks were removed after 3 hours, then the supernatant was collected after filtering using filter paper. The residual content of DBT was determined using gas chromatography and an FPD detector with a retention duration of 8.1 minutes. The following formulae were used to compute the % removal and adsorption capabilities in mgg^{-1}(q_e).

$$q_e = \frac{(C_0 - C_e)V}{M}$$

Where C_o is intial concentration (mg/l) of DBT in model oil

C_e is equilibrium concentration (mg/l) of DBT in model oil

V is the volume of model oil in liter, W is weight of adsorbent in gram.[33]

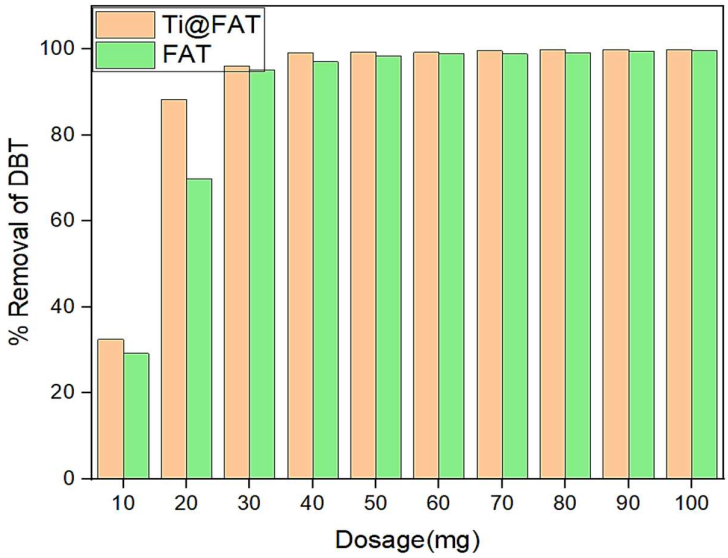


Fig 3.9 % Removal of DBT Dosage Effect of FAT and Ti@FAT

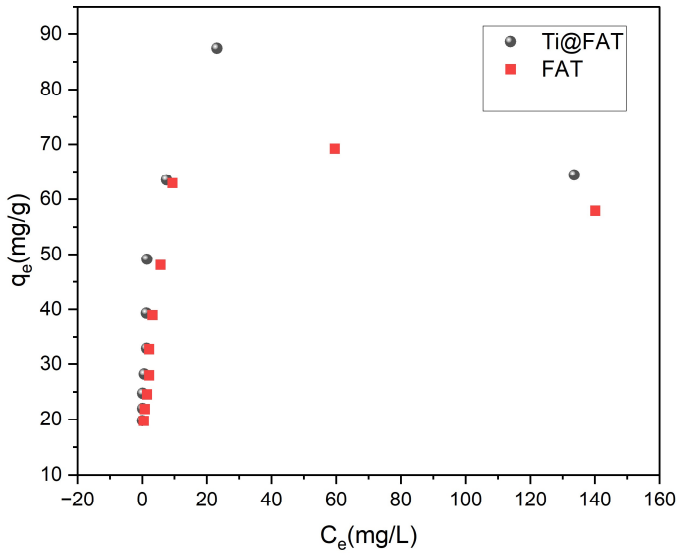


Fig 3.10 Dosage Effect of FAT and Ti@FAT Adsorption Capacity

GC FPD chromatogram of model oil, FAT and Ti@FAT shows the removal of DBT from model oil, Removal efficiency of Ti@FAT is higher than FAT. A maximum removal percentage of 69% and 88% for FAT and Ti@FAT were achieved at 0.02g.$L^{-1}$and maximum adsorption capacity was found to be 64 mgg^{-1}, 57mgg-1 for Ti@FAT and FAT respectively. The FAT modification by Titanium also contributed towards enhancing the removal efficiency. Figure 3.9 and 3.10 compares the effect of dose on the adsorbent capacity and % removal of DBT. The order of the DBT adsorption capacity at the adsorbent surface was as follows:

FAT < Ti@FAT

This sequence clearly illustrates that Titanium treatment boosts the adsorption capacity of FAT

3.4 Adsorption Isotherm Study

The adsorption isotherm analysis provides information on the type and mechanism of adsorbate adsorption at the adsorbent surface.[34] According to this viewpoint, the data collected from DBT batch adsorption investigations were connected by the linear form of the three adsorption isotherms Langmuir, Freundlich, and Temkin.

3.4.1 Langmuir, Freundlich and Temkin Adsorption isotherm

The Langmuir adsorption isotherm explains how adsorbate molecules attach to uniform energy sites on the surface of an adsorbent. The constants q_{max} (mg/g) and K_L (L/mg), as illustrated in Figure 3.11, can be obtained from a plot of C_e/q_e against Ce. The q_{max} value indicates the maximum monolayer adsorption capacity of the adsorbent for specific adsorbates. Meanwhile, K_L (L/mg) reflects the strength of the interaction between the adsorbate and the binding sites, offering insight into the adsorption efficiency. Additionally, the K_L value is useful for calculating the separation factor, R_L, which provides an understanding of how favourable the adsorption process is.

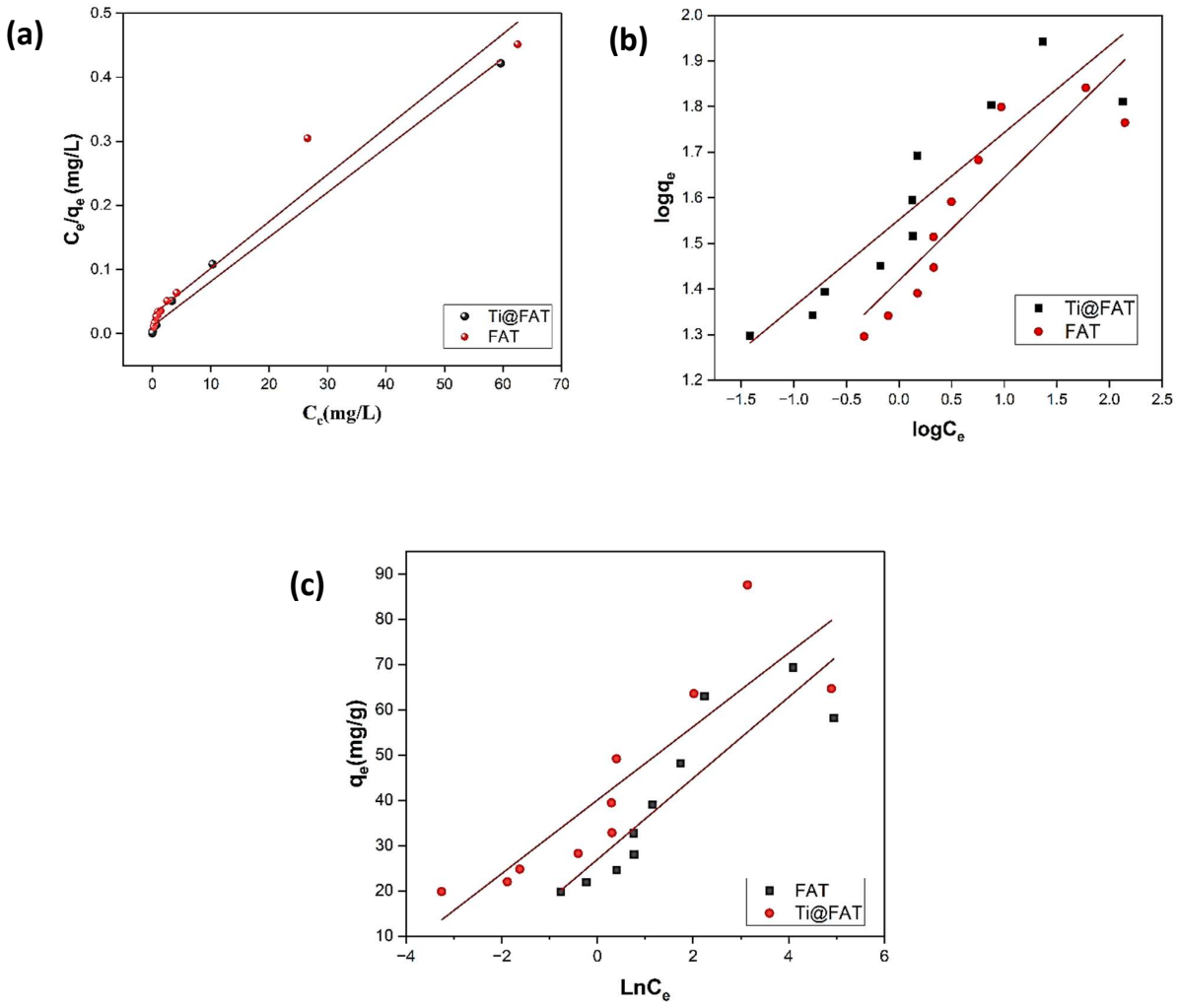


Fig 3.11 (a)Langmuir, (b)Freundlich and (c)Temkin isotherms

Adsorption is regarded as favourable when R_L values fall between 0 and 1, while an R_L= 0 >1 suggests an irreversible process, and values greater than 1 indicate unfavourable adsorption. For DBT on different carbon surfaces, the R_L values were observed to lie within the 0 to 1 range, confirming that the adsorption was favourable under the specified experimental conditions.

The Langmuir isotherm assumes monolayer adsorption onto a homogeneous surface with a finite number of identical sites.[35] The linear form of the Langmuir equation is:

$$q_e = \frac{q_{max} K_L C_e}{(1 + K_L C_e)}$$

Where q_{max} is the maximum adsorption capacity.

K_L is the Langmuir constant related to the affinity between the adsorbent and adsorbate.

The Langmuir plots indicate that both Ti@FAT and FAT follow the Langmuir adsorption isotherm, with Ti@FAT showing improved adsorption capacity and affinity compared to FAT. This suggests that the titanium modification is effective in enhancing the adsorption properties of the FAT adsorbent.

The Freundlich isotherm model suggests that the adsorbent surface contains binding sites with different energy levels. Initially, sites with higher binding energies are occupied, followed by those with lower energies. The adsorption affinity of the adsorbent for the adsorbate is described by the Freundlich constants (K_F) and the heterogeneity factor (N). These constants are determined from the slope and intercept of the $\ln(q_e)$ versus $\ln(C_e)$ graph, as shown in Fig 3.11 They provide insight into both the adsorption capacity and the intensity of adsorption. The 1/N value also indicates how favourable the adsorption process is. Values of 1/N between 0 and 1 suggest favourable adsorption, while values equal to or greater than 1 imply the process is irreversible or unfavourable. According to Table 3.11 Sthe adsorption of DBT on the synthesized materials was found to be favourable. Figure 3.11 presents the adsorption plot based on the Temkin isotherm. The Temkin model, which builds upon the Langmuir isotherm, describes how adsorption on the adsorbent surface increases while the heat of adsorption decreases linearly.

3.4.2 Effect of Contact time of Adsorption of FAT and Ti@FAT

The impact of increasing contact time (5 to 135 min) on DBT adsorption was studied using a 20mg adsorbent in 10 mL (0.02 gL^{-1}) of DBT. The reaction conditions of 30°C and 100 rpm shaking were kept constant. After the experiment was completed, the adsorbents were filtered through filter paper, and the residual concentration of DBT in the supernatant was measured using gas chromatography at 8.1 min retention time.

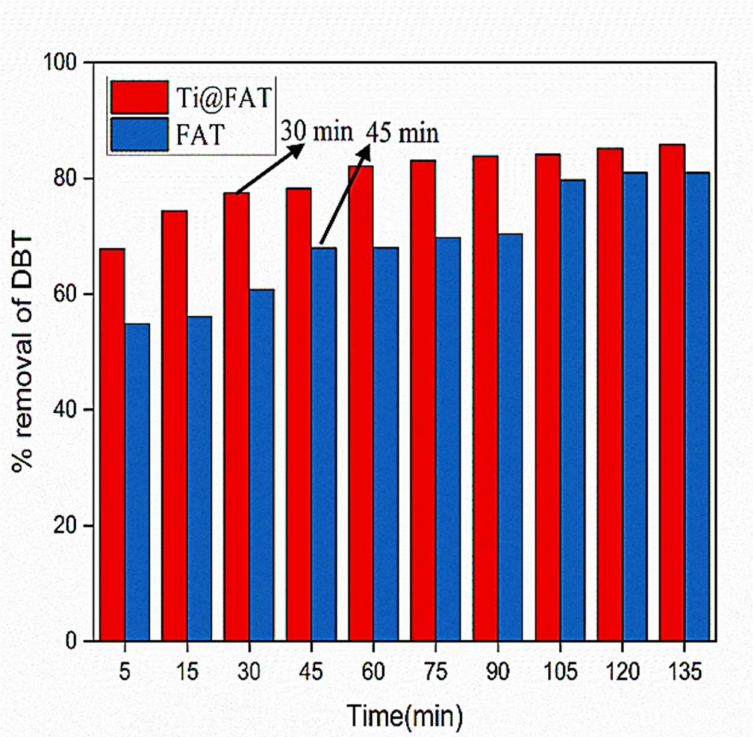


Fig 3.12 Effect of Contact Time on % removal of DBT by FAT and Ti@FAT

At 35 and 45 minutes, the specific values are marked on the graph, highlighting the difference in performance between FAT and Ti@FAT at these times. Ti@FAT reaches a higher removal percentage, close to 78%, while FAT plateaus around 68%. The graph demonstrates that Ti@FAT is a more effective adsorbent for DBT removal compared to FAT, especially at longer contact times.

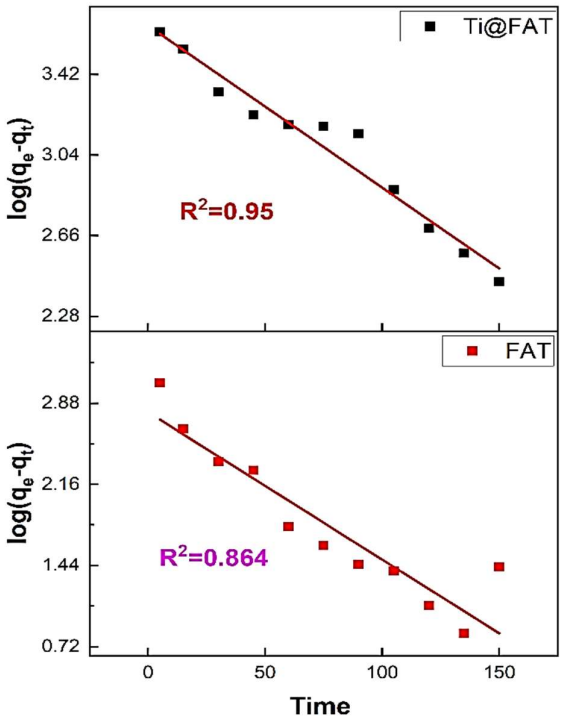


Fig 3.13 Pseudo first order kinetics plot for FAT and Ti@FAT

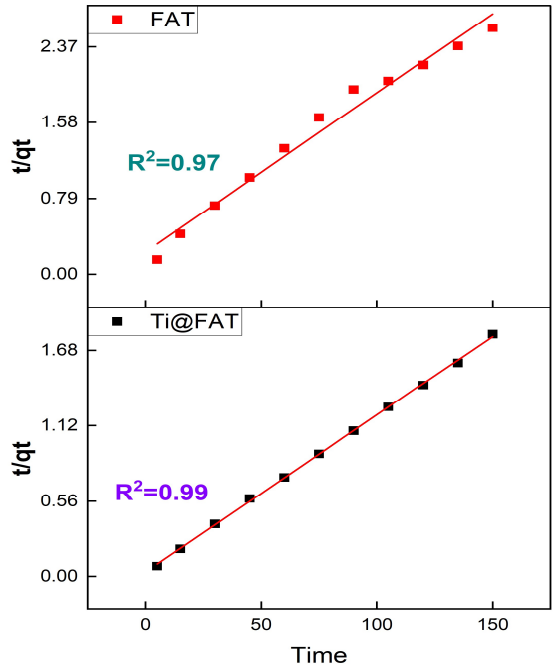


Fig 3.14 Pseudo second order kinetics plot for FAT and Ti@FAT

The high R^2-Values (0.99-1.0) indicate that the pseudo second order kinetics might adequately describe the DBT removal mechanism. Fig 3.14 shows the pseudo second order kinetics show that chemisorption is important in the adsorption of DBT at the adsorbent surface. The rate constants show that DBT adsorbs at a quicker rate. This fast kinetics may prove useful in the industrial use of FAT and Ti@FAT adsorbents. Table 3.2 shows the linear forms of various rate equations and the values of the rate constants.

Table 3.2 Parameter for kinetic model

Kinetics constant	**FAT**	**Ti@FAT**
Pseudo first order		
R^2	**0.86**	**0.95**
slope	**-0.013**	**-0.0076**
intercept	**3.65**	**2.801**
K_l	**-0.0004**	**-0.0002**
Pseudo second order		
R^2	**0.97**	**0.99**
slope	**0.0165**	**0.011**
intercept	**0.033**	**0.235**
K_l	**0.0082**	**0.00051**

3.5 Effect of Temperature of Adsorption of FAT and Ti@FAT

Batch experiments were carried out to investigate how temperature affects the adsorption of DBT onto various adsorbents, specifically at 25^0C, 30^0C, 45^0C and 55^0C. In all tests, the dosages of FAT and Ti@FAT were maintained at 0.02 g/L, while other experimental conditions—such as the initial DBT concentration, model oil volume (10 mL), contact time (30 minutes), and agitation speed (100 rpm)—remained constant. The results revealed that DBT adsorption increased as the temperature decreased, with the highest adsorption observed at 25°C, as shown in Figure 3.15 This trend may be attributed to enhanced diffusion of DBT molecules into the adsorbent's pores at certain temperatures. Additionally, thermodynamic parameters such as changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), derived from the Van't Hoff plot (ln K_D vs. 1/T), were used to further explain the temperature-dependent behaviour of the adsorption process.

Van't Hoff's equation is given in equation

$\ln K_D = \Delta S°/R - \Delta H°/RT$

Where K_D =Distribution Coefficient

T = Absolute Temperature in Kelvin

R= Ideal gas constant (8.314 $JK^{-1}mol^{-1}$)

ΔH and ΔS were calculated from the slope and intercept of the ln K_D versus 1/T plot. Other parameters such as ΔG or $\ln k_D$ were determined using the equation.

$\Delta G° = -RT\ln K_D$

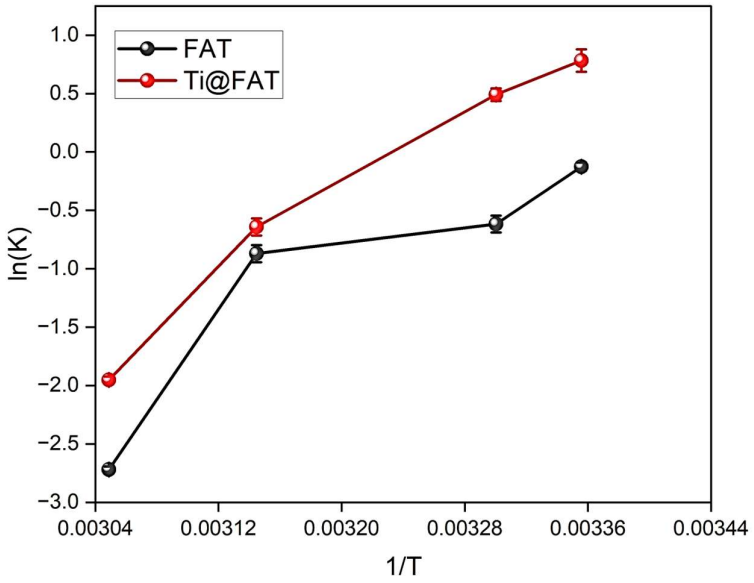


Fig 3.15 Van't Hoff plot DBT adsorption

Table 3.3 parameter for thermodynamic study

Parameters	**FAT**	**Ti@FAT**
R^2	0.94	0.99
Intercept	-28.054	-30.86
slope	8228.84	-30.86
AT 298k **lnK_D**	-2.711	-1.952
ΔG (KJ/mol)	-0.163	-0.351
AT 303K **lnK_D**	-0.617	0.490

ΔG (KJ/mol)	-1.055	-1.356
AT 318K **$\ln K_D$**	-0.870	0.641
ΔG (KJ/mol)	-1.425	-4.319
AT 328K **$\ln K_D$**	-2.718	-1.952
ΔG (KJ/mol)	-2.405	-5.966

3.6 Desulfurization of Multicomponent Simulated Model Fuel

This research evaluates the performance of Ti@FAT in eliminating simulated sulfur compounds from commercial fuel systems. Sulfur compounds are commonly present in fuels used for transportation, including gasoline, diesel, and kerosene. To determine the real-world desulfurization efficiency of Ti@FAT, experiments were conducted using commercially available kerosene obtained from the Nagpur area in India. The sulfur levels in the kerosene before and after treatment were measured using Gas Chromatography with a Flame Photometric Detector (GC-FPD). Calibration of retention times for sulfur compounds in both the multicomponent simulated fuel (MSMF) and kerosene was carried out using standard references for thiophene (TH), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT). An adsorption study was also conducted using MSMF, composed of iso-octane, TH, DBT, and 4,6-DMDBT. The GC-FPD chromatograms were utilized to assess the initial and final sulfur concentrations under optimized conditions of 0.02 g/L of Ti@FAT for 30 minutes. Chromatographic analysis revealed distinct peaks for TH, DBT, and 4,6-DMDBT at retention times of 3 minutes, 8 minutes, and 9.3 minutes, respectively. Based on peak intensities, the remaining concentrations of TH, DBT, and 4,6-DMDBT in the MSMF were found to be 23.7 ppm, 6 ppm, and 7.1 ppm, respectively. The desulfurization efficiency for each sulfur compound was calculated using a specified equation.

$$sulfur\ removal\ efficiency = \frac{intial\ sulfur\ conc(ppm)\ -final\ sulfur\ conc(ppm)}{intial\ sulfur\ conc(ppm)} \times 100$$

The % removal of TH, DBT and 4,6-DMDT is 76.3%, 94% and 92.9%.

A similar desulfurization experiment was conducted using kerosene under optimized conditions. Both untreated and treated kerosene samples were analyzed using GC-FPD, and sulfur concentrations were determined using the specified equation. As shown in the FPD chromatograms (Fig. 3.18), the initial concentration of DBT was measured at 47 ppm. Following the desulfurization process, the remaining DBT concentration is 2 ppm, indicating an approximate removal efficiency of 98%.

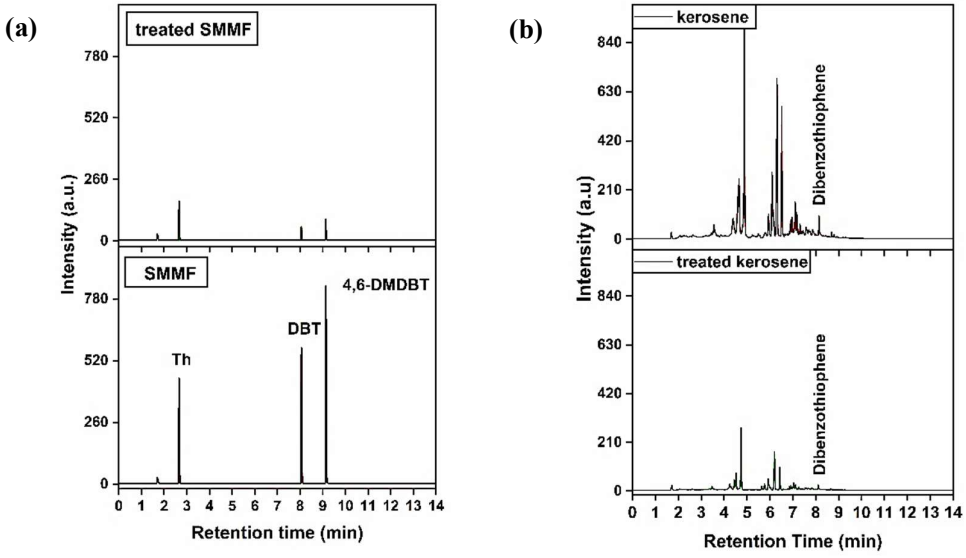


Fig 3.16 FPD Chromatograms of a SMMF and commercial kerosene fuels

Table 3.4 Concentration of Sulfur before and after desulfurization study

Sulfur containing compound	Intial concentration	Remaining concentration	% Removal
TH	53	23.7	76.3
DBT	115.2	6	94
4,6 DMDBT	213.1	7.1	92.9

3.7 Regeneration Performance

Regenerating used adsorbents enhances their efficiency and minimizes secondary waste generation. Effective handling of spent adsorbents during desulfurization is crucial for environmental sustainability. Regenerating spent adsorbents not only extends their usability but also helps prevent environmental contamination and reduces waste generation. Once these adsorbents capture organic sulfur compounds, they may also retain other harmful pollutants that, if not properly managed, could leach into the soil and water, leading to environmental hazards. To mitigate such risks, sustainable approaches such as regenerating and reusing spent adsorbents are essential for restoring their adsorption capacity, minimizing waste, and conserving resources. In our study we regenerated Ti@FAT using toluene followed by a gasification process. This regeneration was carried out at 350°C—above the boiling point of DBT (~335°C)—for 60minutes in an air atmosphere. A shorter treatment duration was selected to reduce potential degradation of adsorption sites due to heat exposure. The regeneration protocol involved 0.02 g/L of adsorbent material, 10 mL of a 200 ppm DBT solution, a 30-minute reaction time, ambient temperature, and agitation at 100 rpm to assess DBT removal efficiency across cycles. This process was repeated three times. As shown in Figure 3.17 Ti@FAT maintained their

desulfurization performance with only a minor decline in sulfur removal efficiency through the fourth consecutive regeneration cycle. In first cycle removal of sulfur is 88.3%, second cycle removal of sulfur is74.29%, third cycle removal of sulfur is 65.5%, in fourth cycle % removal of sulfur is 56.8% and in fifth cycle %removal is 45.4%.

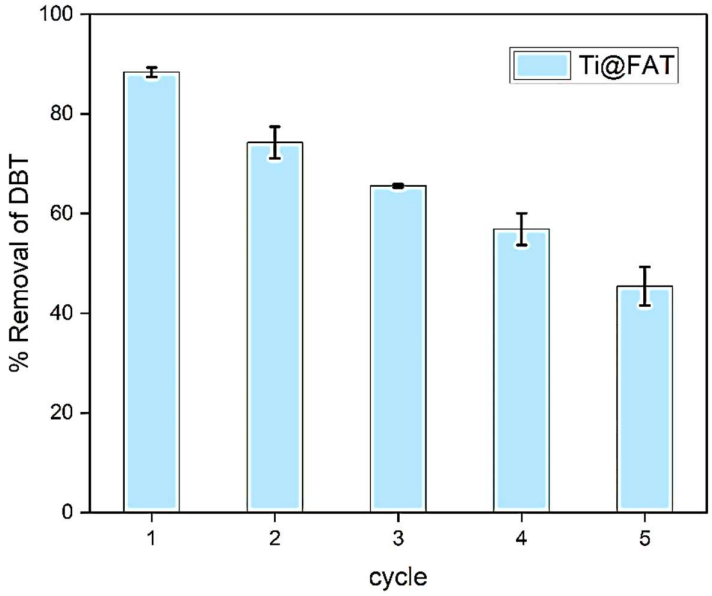


Fig 3.17 Regeneration cycle of Ti@FAT

CHAPTER 4:

CONCLUSIONS

4.1 Conclusions

Activated carbon (FAT) was prepared using *Euryale Ferox* and subsequently modified with titanium to produce Ti@FAT. PXRD analysis revealed that the corporation of Titanium reduced the amorphous character of the FAT. BET surface area measurements showed values of 1095 m^2/g for Ti@FAT, 1400 m^2/g for FAT. The nitrogen adsorption-desorption isotherms indicated a Type II behaviour with a distinct hysteresis loop, confirming the presence of both mesoporous and microporous structures in FAT and Ti@FAT. FTIR analysis verified the presence of various surface functional groups, including –OH, O=C=O, C=C, C–O, on the Ti@FAT. Thermogravimetric analysis (TGA) demonstrated that Ti@FAT exhibited improved thermal stability compared to unmodified FAT. The adsorption performance of FAT and Ti@FAT was evaluated through batch desulfurization experiments. Optimal conditions were established at 40 °C, using an adsorbent dose of 0.02g/L, under agitation at 100 rpm, and a DBT concentration of 200 ppm. The desulfurization capacity for DBT followed the order: FAT (57.8mg/g) < Ti@FAT(64.3 mg/g). The corresponding DBT removal efficiencies from model oil for FAT and Ti@FAT is 69% and 88%. The Langmuir plots indicate that both Ti@FAT and FAT follow the Langmuir adsorption isotherm, with Ti@FAT showing improved adsorption capacity and affinity compared to FAT. The surface binding mechanism of DBT may be explained by the pseudo-second order model, according to the kinetic analysis. As DBT concentration increased, the adsorbents' capacity also increased. The %removal of MSMF which is composed of iso-octane TH, DBT and 4,6-DMDT is 76.3%, 94% and 92.9%. similarly, by using kerosene both treated and untreated samples analysed by using GC-FPD indicating an appropriate removal efficiency of 98%. The surface binding mechanism of DBT may be explained by the pseudo-second order model, according to the kinetic analysis. Euryale ferox-derived carbon is a viable and sustainable precursor for desulfurization adsorbents. Titanium modification significantly enhances adsorption performance, selectivity, and reusability. Ti@FAT presents a cost-effective and green alternative to conventional sulfur removal technologies. Overall, this work contributes to the development of environmentally friendly adsorbents and supports the advancement of cleaner fuel processing technologies.

4.2 FUTURE SCOPE

The current study highlights the potential of Ti@FAT as an effective and reusable adsorbent for fuel desulfurization. However, further research is needed to fully explore and optimize its capabilities. Key directions include:

- Utilizing other underexplored biomass sources for activated carbon production.
- Investigating alternative metal modifications (e.g., Mo, Zn, Fe) and bimetallic systems to improve adsorption efficiency.
- Examining adsorption behaviour in complex fuel systems containing multiple sulfur species and competing contaminants.
- Scaling up the application to pilot- and industrial-level operations under realistic fuel processing conditions.
- Integrating adsorption with hybrid techniques such as catalytic oxidation or ultrasound-assisted processes.
- Conducting long-term regeneration and stability tests under repeated use to evaluate durability and cost-effectiveness.
- Designing scalable, low-cost synthesis methods suitable for commercial implementation.

Advancing research along these lines will support the development of more efficient, sustainable technologies for deep fuel desulfurization.

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